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HYSTERESIS IN SMOG AND FOG DISAPPEARANCE

By

EDWARD Y.H. KENG, CLARA C. WELLONS,
CLYDE ORR, JR.

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I. SUMMARY

The behavior of sodium chloride aerosol particulates under various humidity conditions was investigated. The effects of foreign vapors such as methylamine and sulfur dioxide were studied. A small quantity of methylamine in the aerosol was found to promote condensation on the sodium chloride particulates when the relative humidity was increased and was found to retard evaporation of sodium chloride solution droplets when the relative humidity was decreased. This is because the dew point temperature of the aerosol is increased by the presence of the methylamine. Sodium chloride crystals at a room temperature of 75°F will dissolve into droplets when the dew point temperature of the methylamine-free aerosol is above 66.5°F. This would not occur until the dew point of the aerosol was above 70.5°F when the aerosol contained only 0.1 per cent methylamine by volume. This is because the solubility and the dissolution rate of sodium chloride are retarded by the presence of the methylamine in condensed water.

Evaporation of sodium chloride solution droplets in air containing sulfur dioxide seemed to be slower than in air alone when the concentration was high. No difference was detected on the growth of dry crystals, however. Ethanol vapor and Alpha-pinene did not affect either evaporation or growth for the conditions tested. Aerosols generated from sea water behaved similarly to those generated from sodium chloride solutions.

II. INTRODUCTION

The behavior of atmospheric hygroscopic particulates under varying humidity conditions must be clearly understood if phenomena involved in smog and fog formation and dissipation, cloud and rain drop formation, artificial weather modification and cloud physics in general are to be delineated completely.

Winds blowing over the oceans pick up small salt particles, and a substantial quantity of these are transported over the land[1] from ground level to high altitudes. These salt particles play an important part in smog, fog, and raindrop formation. One such phenomenon which is occasionally noted is the persistence of smogs and fogs after the ambient humidity has dropped below that at which the smog or fog first formed.[2] Some of the droplets comprising these particular smogs and fogs are apparently formed by condensation of moisture on hygroscopic nuclei such as sodium chloride.

Other studies[3,4] have shown that salt particles become droplets essentially immediately when exposed to atmospheres having a relative humidity above 75 per cent. It takes more than 10 minutes for the droplets to be reconverted to crystals if the relative humidity drops to 70 per cent. However, only a few seconds are required to accomplish this at 60 per cent relative humidity. It has been found that the time required for droplets to nucleate into crystals is somewhat longer in contaminated atmospheres than in clean ones. The results indicated that smog and fog consisting at least in part of hygroscopic particulates should persist longer in heavily polluted atmospheres than in clean atmospheres when the ambient relative humidity decreases.

The behavior of solid crystals at low relative humidities can best be explained in terms of gas adsorption theory. It is a well known and documented phenomenon that gas or vapor molecules are adsorbed at the interface between a solid and its gaseous environment, the adsorption being due to the existence of unbalanced intermolecular forces on the surface molecules of the solid. The surface molecules attract other molecules from the environment in order to satisfy these unbalanced surface forces.

The most generally employed theory to describe physical adsorption is that of Brunauer, Emmett, and Teller,[5] ordinarily designated the BET theory. The basic assumption of this theory is that the same forces responsible for the condensation of vapors are also active in the adsorption of gases in multimolecular layers. In a sense it is a generalization of the earlier theory of Langmuir that was limited to adsorption of gas molecules in a single molecular layer.

In the case of a hygroscopic particle, the moisture adsorbed will cause it to dissolve at some relative humidity, which, for a given material at a constant temperature, is only dependent upon the size of the particle. This dissolution will result in an abrupt size increase. If no concentration gradient is assumed across the liquid film adsorbed on the particle, the humidity at which the particle will dissolve may be calculated by assuming the partially dissolved solid nucleus, the adsorbed liquid film of water, and the water vapor in the surroundings to be a three-phase system in equilibrium. The solid particle is assumed in equilibrium with a saturated solution, and the solution, in turn, is assumed to be in equilibrium with the surrounding atmosphere. The liquid film exerts a vapor pressure that is both dependent upon the concentration of the solution and the curvature of the film. The dissolved solid

material will lower the vapor pressure while the curvature of the film will tend to increase it. The relation between particle size, surface energy, and equilibrium concentration for organic solutions is given by the Ostwald-Freundlich equation, which was derived in its most general form by Gibbs[6] from the first law of thermodynamics and the concept of free energy.

In the case of electrically charged particles, Thomson[7] has shown that the effect of potential energy due to the presence of electric charges on a droplet reduces the vapor pressure at the surface. However, the effect amounts to less than one per cent in the case of singly changed droplets of radius greater than 2×10^{-3} micron. Since the correction is inversely proportional to the square of the radius, it is taken to be negligible here.

The behavior of solution droplets with change in relative humidity was first described quantitatively by Köhler in 1921. A modified derivation was obtained by Wright in 1936[8] by adding a correction to the general equation of Kelvin as applied to pure water for the vapor pressure lowering due to the presence of the solute. In this development Wright assumed the ratio of the vapor pressure depression to the vapor pressure over a plane surface of solution was proportional to the concentration of the solution and that the constant of proportionality, which was called the hygroscopic factor, was independent of the solution concentration and only dependent upon the chemical species of the solute.

Numerous investigations have been made into the likelihood of atmospheric particles, especially hygroscopic ones, serving as nuclei for the formation of smog and fog.[4,9,10] It has also been noted that the concentrations of smoke, sulfur dioxide, etc., in city areas during dense

fog can rise to several times normal values.[11,12,13] There is, however, little knowledge of the relationship between condensation and nucleation processes involving hygroscopic nuclei and the surrounding atmospheric composition and relative humidity.

The behavior of condensation nuclei under changing humidities has been studied by many investigators.[14,15,16,17] Nuclei size was determined by an ion counter when the nuclei had radii from 0.01 to 0.1 micron and size was determined photographically when the nuclei had radii between 2 and 25 microns. This work was done, however, in the absence of any organic or inorganic contamination.

The presence of certain vapors inhibits the nucleation of supercooled water droplets with freezing nuclei. Vonnegut[18] found that a minute amount of alcohol vapor could alter the shape of growing ice crystals by inhibiting growth in certain directions. Kabayashi[19] also found that traces of silicone or acetone vapor affected the form of ice crystal growth. Reynolds et al.[20] reported that ammonia increased the effectiveness of silver iodide as a nucleating agent under some conditions but decreased the effectiveness under others. A comprehensive study by Birstein[21,22,23] in which the effects of several vapors on nucleation by silver and lead iodide showed that the effectiveness of both was inhibited by various amines and ammonia, but not by isobutane, diethyl ether, n-heptane, bromobenzine, and ethylene glycol. Concentrations of the order of 1 ppm of ethylamine in the carrier gas decreased the temperature of ice nucleation on lead iodide by 7°C and higher concentrations caused even greater decreases in the nucleation temperature.[23] It was found[24] that ethylamine and turpentine decisively lowered the temperature at which water drop freezing occurred; other chemicals tested had little or no effect. Observations of

the behavior of natural atmospheric aerosols under conditions of varying humidity led Goetz[25] to suggest that the adsorption of minute quantities of organic vapor would be a limiting factor for the evaporation of water. Unfortunately, no information has been reported to our knowledge on the specific behavior of condensation nuclei in a contaminated atmosphere.

III. EXPERIMENTAL INVESTIGATIONS

Sodium chloride particles were used in this study. The procedure of the investigation was very similar to two previous studies[3,4] in which only clean air was used. Modifications, however, were made at many places. Foreign vapors used were mainly methylamine and sulfur dioxide. Other gases such as ethyl alcohol and ethylamine were only used for limited tests.

A. General operation

A schematic diagram of the equipment is presented in Figure 1. Numbers on Figure 1 indicate components as follows: 1. air filter, 2. pressure regulator, 3. atomizer, 4. entrainment separator, 5. small particle separator, 6. large particle remover, 7. humidity control chamber - saturated LiCl solution, 8. humidity control chamber - concentrated phosphoric acid, 9. foreign vapor supply, 10. dry crystal conditioning chamber, 11. solution droplet conditioning chamber, 12. residence chamber - 15 seconds residence time, 13. residence chamber - 1 to 4 minutes, 14. residence chamber - up to 37 minutes, 15. flowmeter, 16. ion counter, 17. foreign vapor remover, 18. dew point indicator, 19. micro-microammeter, 20, power supply, and 21. recorder. An aerosol of sodium chloride droplets was generated by atomizing a dilute salt solution with a Devilbiss No. 180 atomizer having its container and impaction plate enlarged so that operation could be continued for an entire 8-hour day without refilling. The larger impaction plate also eliminated intermittent surges by stopping the larger droplets from collecting in the output tube. Two devices were employed to sharpen the size distribution of the particulates so that a narrow range of sizes could be obtained. One was a coaxial electrostatic precipitator capable of collecting essentially all particulates smaller than 0.01 micron in radius. The other was a

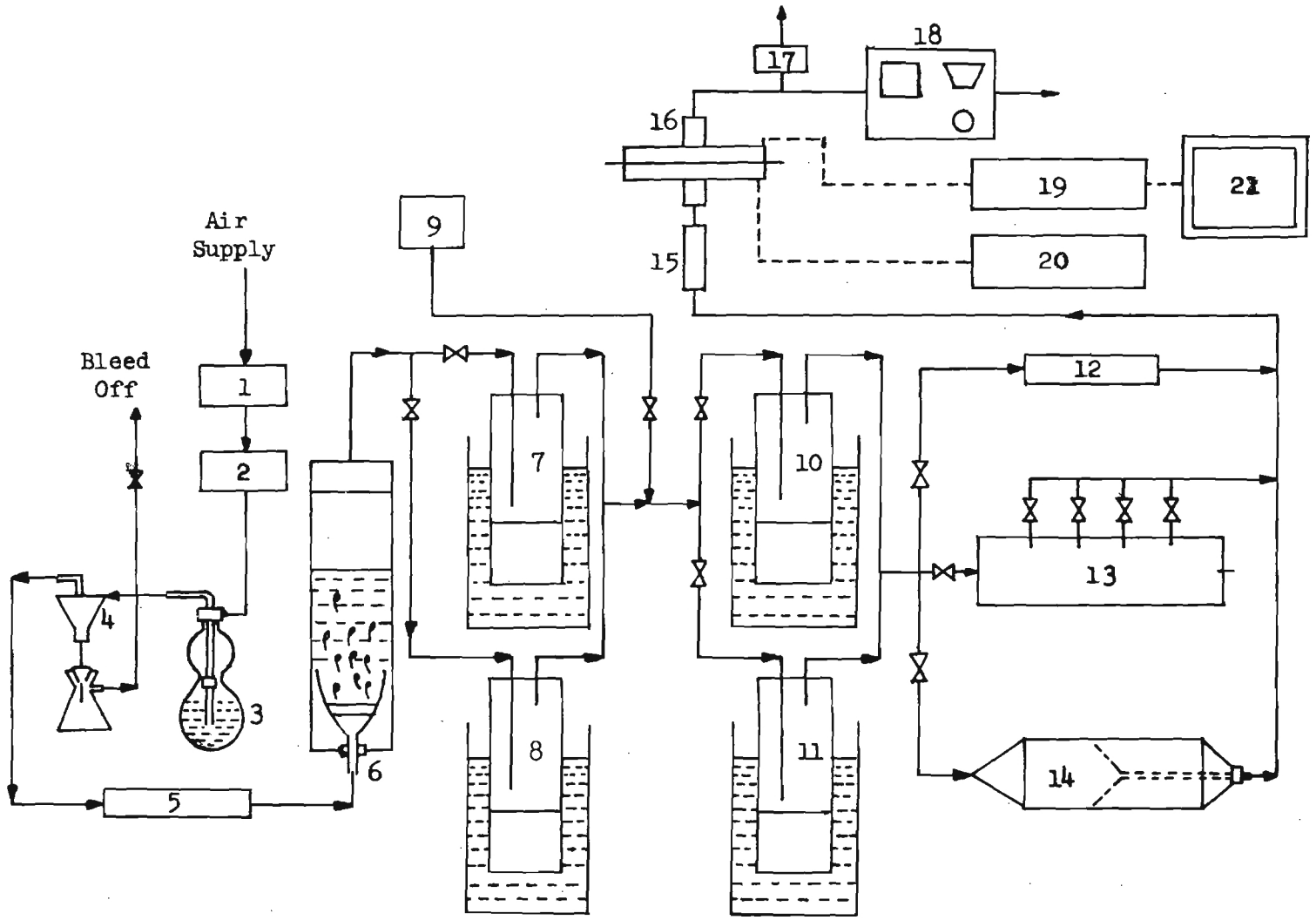

Figure 1. Schematic Diagram of Equipment.

vertical column of water through which aerosol was bubbled. This latter device removed essentially all particulates larger than about 0.05 micron in radius. The aerosol moisture content was controlled by passing portions of the aerosol through two chambers, one chamber partially filled with saturated LiCl solution and the other with concentrated phosphoric acid. Foreign vapors were added to the aerosol before it was introduced into either of two other conditioning chambers. These were immersed in constant temperature water baths. The temperatures could be set to produce either dry crystals or solution droplets in an atmosphere of 95 per cent relative humidity. The aerosol was led to one of three residence chambers. One gave a 15-second residence time; one gave 1 to 4 minutes at 1 minute intervals; and the other gave up to 37 minutes. The particulate size distribution was measured immediately after the aerosol emerged from a residence chamber by means of a parallel-plate, radial-flow ion counter.[3] The size distribution indicated by the ion counter was repeatedly checked using micrographs to insure accuracy. The dew point temperature was measured by a Cambridge Systems Thermoelectric Dew Point Hygrometer, Model 990-B. Details of each component, or set-up, are discussed in the following section.

The micro-microammeter and the power supply were kept on (on standby status) at all times to insure operation without drift. The dew point indicator, using all solid state components, could be turned off when it was not needed. To start a test, the valve of the air supply was opened and the pressure was adjusted to 12 psig. With the aerosol flowing, water was let into the column of the large-particle remover up to a level of 15 inches. The desired aerosol flow rate of 7580 cm^3 per minute was finally obtained by controlling the micrometer needle valve. Most of the tests

were made using the 1- to 4-minute residence chamber. Half of the aerosol was withdrawn from one of the four outlets located at the side of the residence chamber for size measurement. The other half of the aerosol was exhausted. Dew point temperature was measured before the aerosol was released to the room or directed to the foreign vapor remover.

B. Description of the apparatus

1. Aerosol generation equipment

A Devilbiss, No. 180, liquid nebulizer was used to generate an artificial fog from a dilute sodium chloride solution (0.05% by weight). The standard nebulizer bottle was replaced by a larger one redesigned to insure sufficient solution for operation over periods of 10 hours without refilling. The nebulizer itself operated on the Venturi principle and was provided with an impaction plate in the droplet stream. This original plate was replaced by a larger one that was capable of collecting and returning to the main body of solution nearly all large droplets; otherwise they would be collected in the output tube and produced intermittent surges. Satisfactory performance was obtained by operating the nebulizer with a constant pressure differential of 12 psi. The air was water- and oil-free and was passed prior to use through a filter consisting a 5 inches of firmly packed felt. Millipore filters were employed just before the air entered the nebulizer to insure no lint or dust from the filter could enter the system. The nebulizer was immersed in an ice bath during operation in order to reduce solution evaporation. The fog produced had a relative humidity of about 30 per cent at room temperature, hence the aerosol was composed completely of NaCl crystals shortly after generation.

A micrometer needle valve was provided on the downstream side of the nebulizer to bleed off excess aerosol. By careful adjustment of this valve a constant aerosol flow rate was obtained through the remainder of the apparatus. An aerosol flow rate of 3790 cm^3 per minute through the ion counter was employed since it was found that this yielded the most satisfactory operation of the instrument.

2. Equipment for sharpening the size distribution of the aerosol

Upon leaving the nebulizer the aerosol flowed directly into an entrainment separator. It was a glass, cyclone-shaped separator. Its purpose was to remove large droplets which were not collected by the impaction plate in the nebulizer from the aerosol stream. Thus these large droplets were not able to enter the system tubing there possibly to stick on the tubing side; rather, a smooth, uniform flow was insured.

A small ion remover was designed to precipitate the fraction of aerosol particulates smaller than 0.01 micron in radius. It consisted of a stainless steel tube 15.5 inches long having an internal diameter of 0.80 inch. A brass rod 0.25 inch in diameter and 12.25 inches long was mounted co-axially by means of perforated Teflon insulators. The inner rod was installed so that an entrance length of 1.50 inches was provided. The exposed length of the inner rod was 11.75 inches. By applying a constant electric potential of 90 volts between the inner rod and the outer stainless steel tube an electric field was obtained which collected particulates smaller than 0.01 micron in radius at an aerosol flow rate of 3790 cm^3 per minute.

The aerosol was made to flow from the entrainment separator through the small ion remover and then to bubble through a water column 15 inches

high. A Büchner-type filter funnel of 80 millimeters internal diameter having a coarse-porosity glass support was installed at the bottom of a plexiglass tube 48 inches long and having an internal diameter of 4 inches. By passing the aerosol through the glass support, discrete, even-sized air bubbles were obtained. This bubbling procedure removed particulates larger than about 0.05 micron in radius from the aerosol stream. The filter funnel had to be cleaned every other week to prevent bacterial growth in its pores even though the water in the column was changed everyday.

3. Humidity control chambers

The humidity of the aerosol was controlled by two chambers which were placed in parallel and were immersed in a temperature-controlled water bath. One chamber contained a saturated solution of lithium chloride and the other concentrated phosphoric acid. The relative humidity of the aerosol was below 50 per cent after passing through the former chamber and above 80 per cent through the latter one at room temperature. The relative humidity of the aerosol could be obtained at any value in between by adjusting the ratio of the aerosol flow into the two chambers. The two chambers were made identical so that the aerosol particles lost in the chambers, if any, should be identical.

Almost any desired humidity conditions could be obtained with the two chambers at room temperature. If higher or lower humidity than either one of the chambers could normally produce was desired, the temperature of the bath was adjusted until it was obtained. In this case, only one chamber was used. When intermediate humidity conditions were desired, the two chambers were used simultaneously.

These two chambers were employed in parallel instead of in sequence as in previous studies.[4] Much shorter time was required to achieve a new humidity condition with this arrangement. The aerosols were directed into one path immediately as they emerged from the chambers through a "Y" joint.

4. Introduction of foreign vapors

Methylamine and sulfur dioxide were stored in pressurized tanks. Only one gas was used at a time. The flow rate was controlled by a regulator, a micrometer valve, and a rotameter (tube No. 601, series No. R-2-15-AA, Matheson Co., Inc.). The rotameter had two floats; one was of stainless steel and one was of pyrex glass. The rotameter was calibrated and checked frequently by the movement of a soap film in a buret. When reproduction of a desired flow rate was difficult to achieve, the rotameter tube and the balls were cleaned. A smaller rotameter tube, No. 600, was not used because frequent cleaning was required with it. A flow rate down to 4 cc/min could be measured accurately with tube No. 601 provided the tube and balls were clean.

Foreign gas was introduced into the aerosol before it entered the conditioning chamber. Tests were made after steady state was achieved. When methylamine was introduced into the system, the dew point temperature would rise. Tests were made after the readings of the dew point indicator were steady again. A 5-minute waiting period was usually necessary for methylamine.

5. Humidity conditioning chambers

Humidity conditioning chambers were used to adjust the aerosol to a desired condition--either containing all dry crystals or all solution

droplets--before it entered the residence chamber. Therefore, the initial conditions of the aerosol in the residence chamber were uniform and identical for similar tests.

The low humidity conditioning chamber consisted of an empty reservoir immersed in a constant temperature water bath. The bath was a Magni-whirl Refrigerated Water Bath, Model No. MR-3220-A, manufactured by the Blue M Electric Co., Blue Island, Ill. This instrument operated from $0^{\circ}C$ to $100^{\circ}C$ with control to $\pm 0.1^{\circ}C$. The unit was also provided with an automatic, electromagnetically actuated stirring device. It was found, however, that this device introduced a very high level of disturbance on the current readout of the ion counter. Therefore, the stirring mechanism was disconnected and a stirrer operated by an electric motor was used instead. The purpose of this chamber was to force the aerosol to achieve an equilibrium state at a low humidity condition. Therefore, when the temperature of this chamber was much higher than the dew point of the aerosol, a low local relative humidity level was obtained and the aerosol particulates all became dry crystals. The temperature of this low humidity conditioning chamber was set at approximately $45^{\circ}C$. This temperature was sufficiently high to convert all particulates into dry crystals for all test conditions.

The high humidity conditioning chamber also consisted of an empty reservoir of the same type as before but it was immersed in a separate temperature-controlled water bath. The water bath used was a Hi-Lo Temperature Bath, Model No. 832, manufactured by the Wilkens Anderson Company, Chicago, Ill. This device employed a direct-action mercury thermostat switch which could be adjusted. The range of operation of the unit was from about $0^{\circ}C$ to above $50^{\circ}C$ and the precision of the temperature

control was also ± 0.1°C. The temperature of the high humidity conditioning chamber was always adjusted to be slightly higher than the dew point temperature of the aerosol. The temperature was kept at such a level that the humidity of the aerosol inside the chamber for each test was always at 95 per cent relative humidity. Thus all tests involving the size behavior of solution droplets had identical initial condition.

The high humidity conditioning chamber and the low humidity conditioning chamber were connected to the system by means of two, two-way stopcocks. The stopcocks were switched depending on whether dry crystals or droplets were required by the particular experiment. The aerosol coming from the conditioning chamber flowed through a thin-wall glass tube of small diameter. Therefore, the temperature of the aerosol from either conditioning chamber would fall to within less than half of a degree from room temperature. The residence time in the tubing was about 3 seconds; it was not included in the residence times presented in the results.

6. Residence chambers

Three residence chambers were built into the system and one was used at a time. The smallest one was a 1000-ml, 3-neck, round-bottom flask. The average residence time of the aerosol in it was about 15 seconds at a flow rate of 3790 cm^3/min. A thermometer was located in the chamber and the indicated temperature was used to evaluate the relative humidity inside the chamber. This temperature was usually within half a degree of the room temperature.

The medium-sized residence chamber was a glass pipe with a diameter of 9.53 cm and a length of 242 cm. Aerosol could be withdrawn from any

of eight outlets along the side of the chamber simply by opening the appropriate stopcock. In this study, only the four outlets with 1-minute intervals were used. Those of half-minute intervals were plugged except for one in which a thermometer was installed. The aerosol at a flow rate of 7580 cm^3/min entered the chamber at one end. A restriction was used to prevent the aerosol from flowing directly into the chamber from a small entrance. The restriction consisted of a plexiglass cylinder having a diameter of 5 cm and length of 0.6 cm; the end of the cylinder was closed. Sixteen holes 0.3 cm in diameter were drilled through the wall of the cylinder. Only little turbulence was created inside the chamber after this device was installed. Half of the aerosol was withdrawn from the chamber from an exit where a desired residence time was achieved. The other half of the aerosol flowed through the entire chamber and was exhausted at the end. A steady state could be obtained quickly when a test requiring a new residence time was switched with this arrangement. Two-way and three-way stopcocks were installed along the exits of the residence chamber so that any of the exits could be opened and closed easily.

The large residence chamber was made of stainless steel. It consisted of two concentric, close-fitting cylinders terminating in 30° cones. This chamber provided residence times greater than 4 minutes. Details of this residence chamber were given in a previous report.[4]

7. The ion counter

The ion counter consisted essentially of two, flat, circular, parallel plates separated a fixed distance. The plates were mounted inside a metal enclosure and insulated from it with Teflon insulators. The lower plate

was fixed to the lower part of the enclosure and the upper plate was suspended at three points from the upper part of the enclosure. The separation between the plates was adjusted by raising or lowering the upper plate. The aerosol was admitted through the center of the lower plate and was made to flow radially outward. Details of construction are given in Figure 2 and by a schematic diagram in Figure 3.

The flow rate was adjusted to obtain laminar flow conditions. The plates were maintained at a fixed, but adjustable, potential difference, and, therefore, the charged aerosol particulates when flowing radially outwards between the plates were subjected to an electrical force which tended to move them toward one of the plates according to the nature of their change. A Keithley Regulated High Voltage Power Supply, Model 241, was employed to fix the potential. This instrument had a range of from 0 to 1000 volts at up to 20 milliamperes, and its voltage output could be adjusted in powers of 10 from -2 to +2 with five calibrated panel switches. The accuracy of the output was 0.05 per cent with a stability of 0.005 per cent per hour. The lower plate was operated as the negative electrode so that it collected the positively charged particulates although the polarity could have been reversed. The results would not have been different, for aerosols generated by nebulizing electrolyte solutions are very nearly electrically neutral and therefore have equal number of positive and negative charges.

A Keithley, Model 410, Micro-Microammeter was used to measure the ion current generated by the deposition of the charged particulates upon the upper plate of the ion chamber. The micro-microammeter was a line-operated vacuum tube electrometer designed to measure currents from 10^{-3}

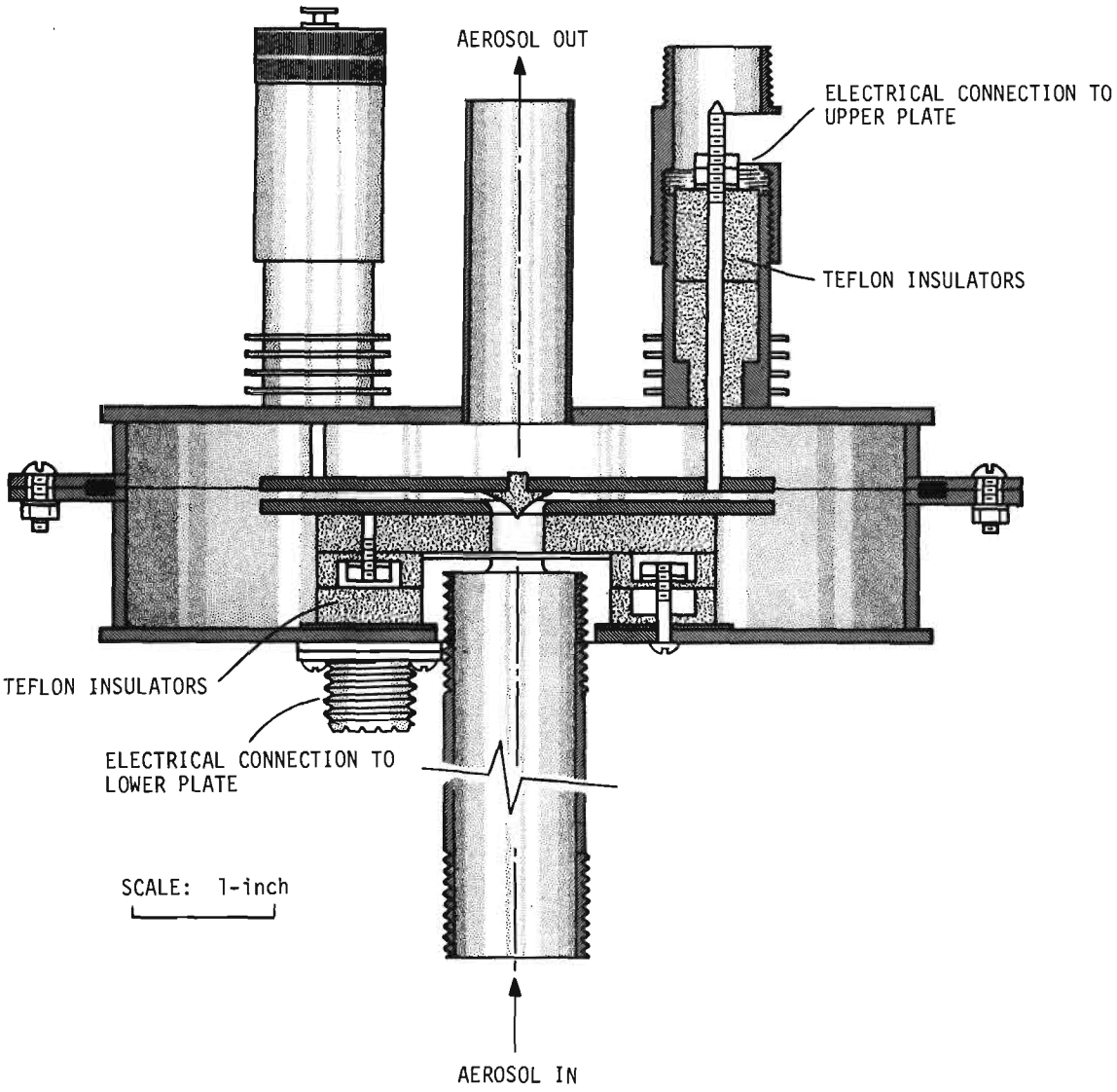

Figure 2. Constructional Details of the Ion Counter.

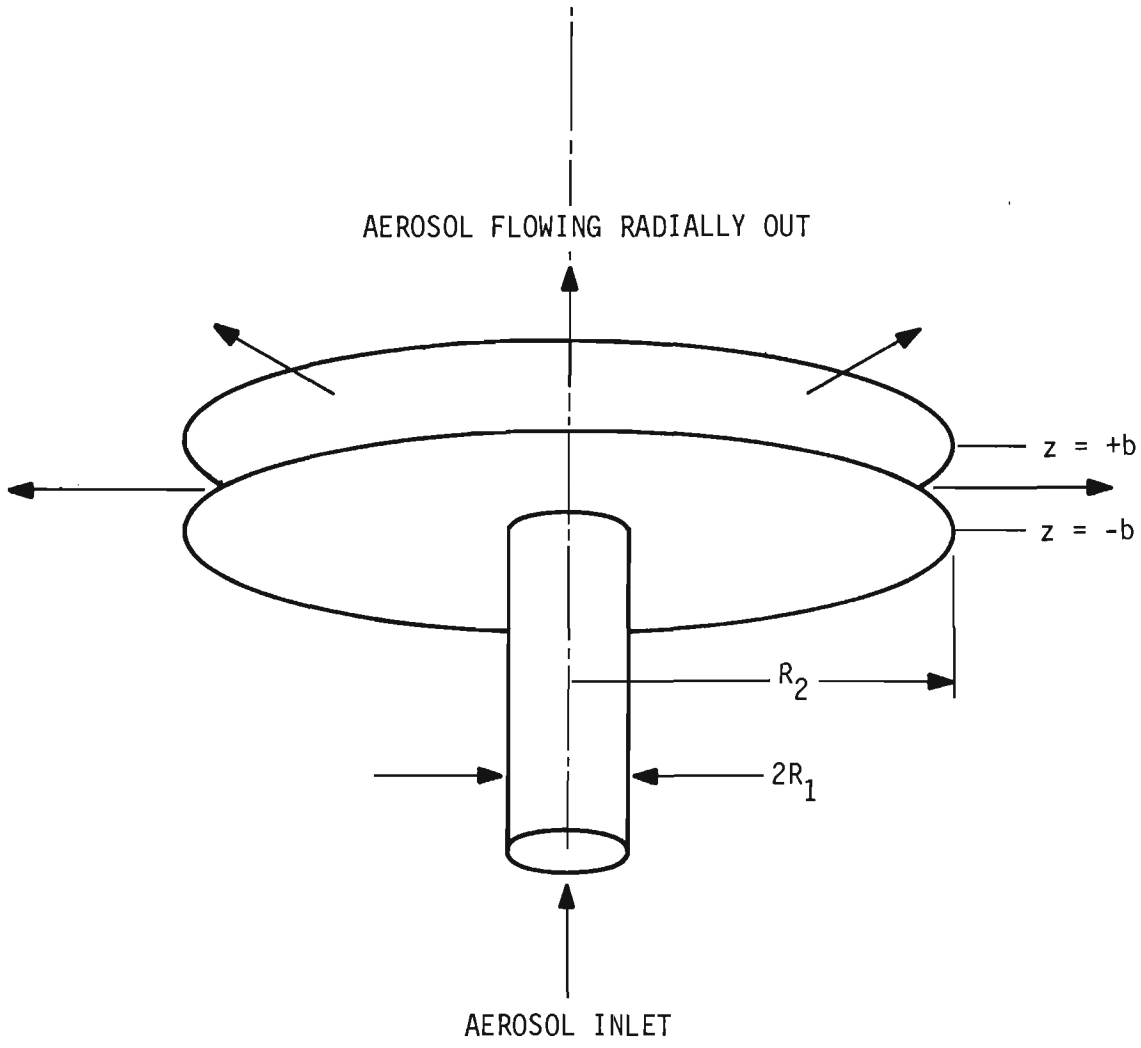

Figure 3. Schematic Diagram of the Ion Counter.

to 3×10^{-13} ampere. It had a zero drift of less than 2 per cent of full scale in eight hours.

For each fixed potential difference a certain fraction of the charged particulates was collected. This fraction increased with the ion chamber plate voltage until all the charged particulates were collected. Low-noise, coaxial cable was used to connect both the lower plate of the ion counter to the power supply and the upper plate to the micro-microammeter. This was especially important in the second case since the cable even had to be tied down firmly to avoid vibrations which induced electrostatic effects readily detectable by the micro-microammeter. Eliminating electrical noise constituted one of the most difficult problems in all of the experiments.

In order to prevent condensation of moisture on the Teflon insulators of the upper plate supports, electrical heaters were built in to keep these components about $10^{\circ}C$ above from room temperature. A variable transformer supplied power continuously to the heaters at approximately 15 volts. In order to keep the leakage current down to an acceptably low value, the resistance between the plates of the ion counters had to be held at or above 10^{16} ohms. After several weeks in use it was found necessary to disassemble the ion counter and clean the various components, especially the Teflon insulators. A final rinsing with absolute ethanol and drying in a laboratory oven for several hours at $80^{\circ}C$ generally proved adequate. Warm potassium dichromate-sulfuric acid cleaning solution was used on the Teflon insulators for a few minutes in order to dissolve stubborn contamination.

8. Hygrometer for dew point measurement

A continuous reading of the aerosol dew point was made by sampling a fraction of the aerosol stream as it emerged from the ion counter. A Cambridge Systems Thermoelectric Dew Point Hygrometer, Model 990-B, was used for this purpose. This instrument determines the temperature at which condensation begins to form (dew point) upon a rhodium-plated, thermoelectrically cooled silver mirror by detecting the change in reflectivity. The instrument detects and automatically controls the temperature of the mirror at the dew point of the aerosol. The mirror was provided with an embedded, aged, precision, thermistor, temperature sensor which allowed direct dew point temperature readout over a wide-scale, taut-band meter calibrated in both Fahrenheit and Centigrade scales. The operating range of the instrument was from a frost point of $-40^{\circ}F$ to a dew point of $80^{\circ}F$. This range permitted measurement of relative humidities from 3 to 100 per cent at an ambient temperature of $80^{\circ}F$. The applicability of this instrument to aerosols is especially appropriate since the instrument was quite insensitive to deposition of particles on the mirror surface. It was found that the instrument could be used over a period of several weeks without cleaning the mirror surface. It was found also that, if the mirror surface was cleaned after such a period of usage, the new reading would be closer to the previous one than the quoted accuracy of the instrument. A flowmeter was attached at the exit of the hygrometer to make sure that the flow rate was always satisfactory and constant.

9. Equipment for removal of foreign vapors

All aerosols containing foreign vapors were finally directed to a 5-gallon glass bottle which was filled with about 4 gallons of water. The

aerosol was bubbled through a tube at the bottom of the bottle. When methylamine was used, sulfuric acid was added to water to promote absorption. A pump was used to transport the exhaust gas to the atmosphere. Sodium hydroxide was added to the water to absorb sulfur dioxide gas. Absorption agents were added as needed.

IV. COLLECTION AND TREATMENT OF DATA

After all the components were readied and a constant aerosol flow rate was achieved, the humidity was adjusted until the desired value was obtained. The aerosol from a selected residence chamber was led into the ion counter for size measurement. The voltage applied to the ion counter was regulated by the power supply and the ion current generated was recorded. A complete size spectrum analysis usually could be obtained in the range from 20 volts to 500 volts, but the voltage was always applied to higher values to insure a maximum current I_{max} that was steady and correct.

Aerosol without contaminant was tested first. If the operation was satisfactory, foreign vapor was then added to the system at a constant flow rate. The voltage and current data were recorded and then plotted.[26] An example of a set of data is given in Figure 4. A tangent line drawn from the point ($I = 1/2\ I_o$, $V = 0$) to the data curve and the point where the tangent line and the data curve meet has coordinates of (I_{mean}, V_{mean}). The value of r_{mean} is the value of r_o at the correspondent value of $V_o = V_{mean}$ as shown on Figure 6. This mean size was employed in the ultimate analysis as the size of the aerosol particulates. If a complete size spectrum analysis was needed, usually ten selective points at various values of V_o were used. The value of $G(r)$ as obtained by Equation 1* represents the fraction of particulates (on counts or number basis) less than the size r_o at respective values of V_o.

The aerosol temperature in the residence chamber and the dew point temperature measured before and after a test were recorded and then used to evaluate the relative humidity at which the aerosol particulates were

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* Presented subsequently

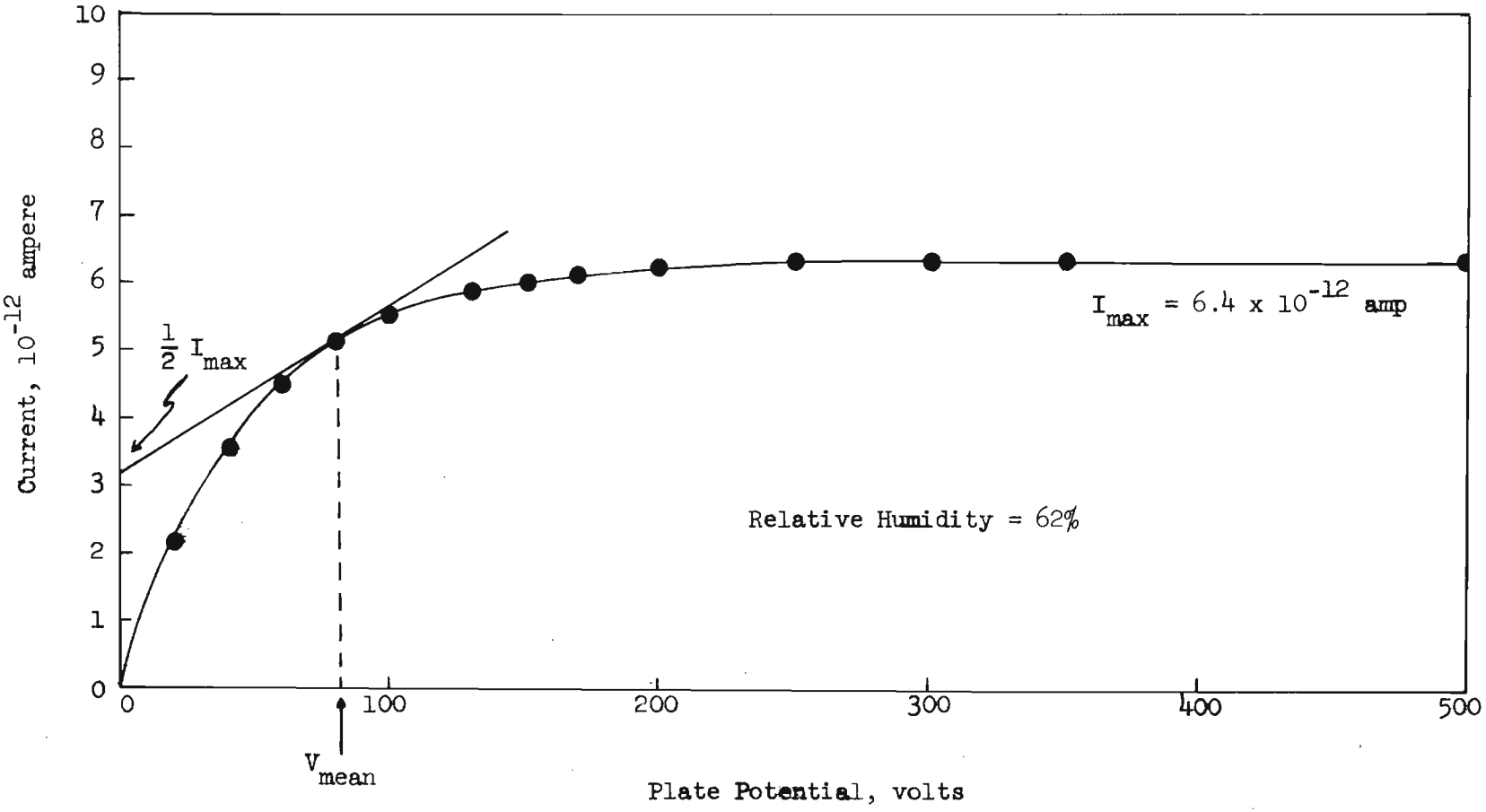


Figure 4. Analysis of Ion Counter Data for Determining Mean Radius of Particulates.

aged. Data were discarded if the temperatures before and after a test were noticeably different.

Two initial conditions of the aerosol particulates have been studied. One was the dry-crystal condition and the other the solution-droplet condition. Dry-crystal conditions were employed to study the growth rate of dry sodium chloride crystals when they were exposed to higher relative humidity atmospheres. Solution-droplet conditions were employed to study the evaporation rate of solution droplets when they were exposed to lower relative humidity atmospheres. Either of the initial conditions were held the same for all similar tests and the aerosol temperature was always at about the room temperature when the aerosol entered the residence chamber.

The concentrations of foreign vapor used in this study are all volumetric concentrations; for example, 0.001 methylamine means 1 ml of methylamine in 1000 ml aerosol. Residence time is the time used to age the aerosol of indicated dew point temperature in the residence chamber where the temperature was recorded. This temperature is very critical to the growth and evaporation of particulates. The reason the dew point temperatures of the aerosol were used instead of relative humidities is because even a small quantity of methylamine in an aerosol increases the dew point temperature. The relative humidity is not known if a reaction occurs between the water and the added vapor. It is, of course, the same according to the definition if no reaction occurred and very little vapor was added.

V. COMPARISON OF PARTICLE SIZE MEASUREMENTS

A. Comparison of ion counter and micrograph data

The size of the aerosol particulates was mainly measured by ion counter in this study. The technique and theory developed by Hurd and Mullins[26] were employed. The frequency distribution function has been given by them as

$$G(r) = \frac{1}{I_{max}} \left(I_o - V_o \frac{dI_o}{dV_o} \right) \qquad (1)$$

where I_o is the total current obtained for the amount collected at the voltage V_o and I_{max} is the maximum current obtained when the entire distribution was collected.

A graphical procedure for evaluating the frequency distribution function $G(r)$ is illustrated in Figure 5. Values of $G(r)$ at corresponding values of V_o thus can be obtained. The relation between plate voltage V_o and the maximum particulate size collected r_o at that voltage has been determined for several conditions by Hidalgo.[4] The curve presented in Figure 6 is interpolated from these results for the conditions used in the study.

The particulate size r_o collected at the plate voltage V_o is very sensitive to the distance between the two plates of the ion counter. An error in the measurement of the distance could result in a significant error in the size measurement.

Aerosols containing all dry crystals of NaCl were employed to compare the particulate size measurements by ion counter and electron microscope.

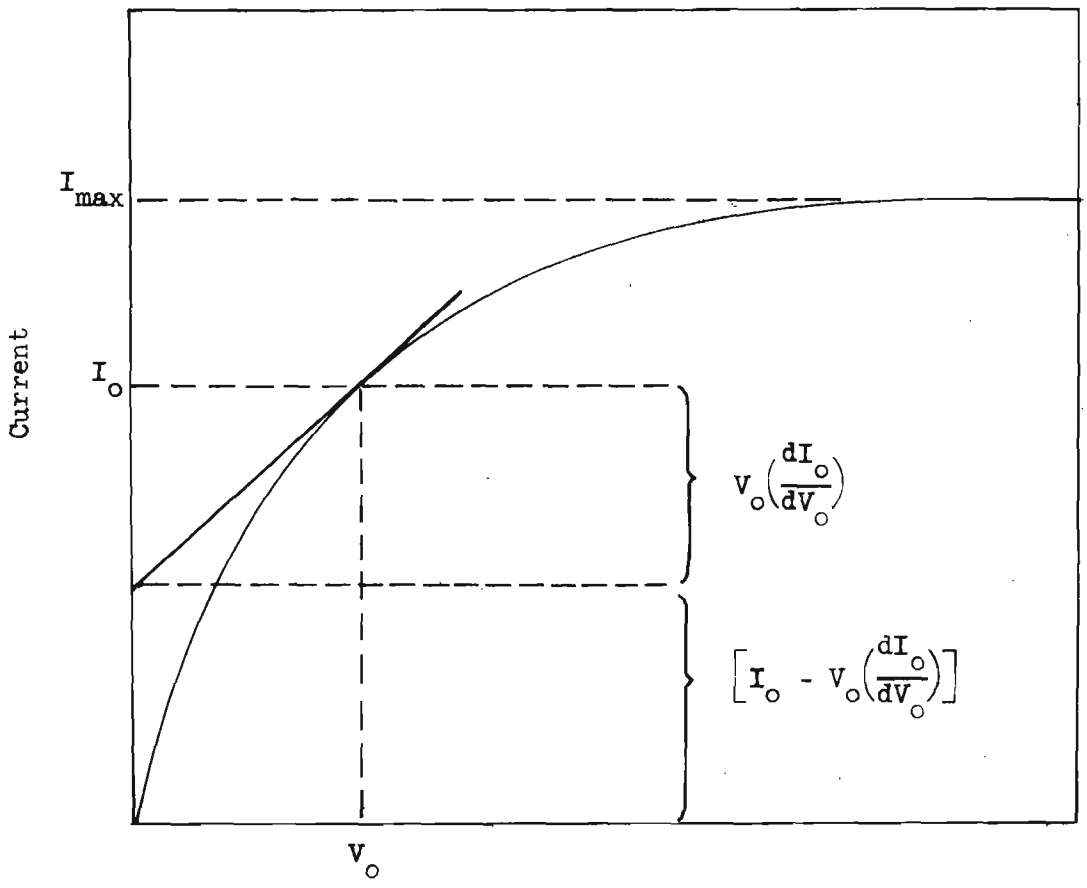


Figure 5. Evaluation of Frequency Distribution Function for Ion Counter Measurements.

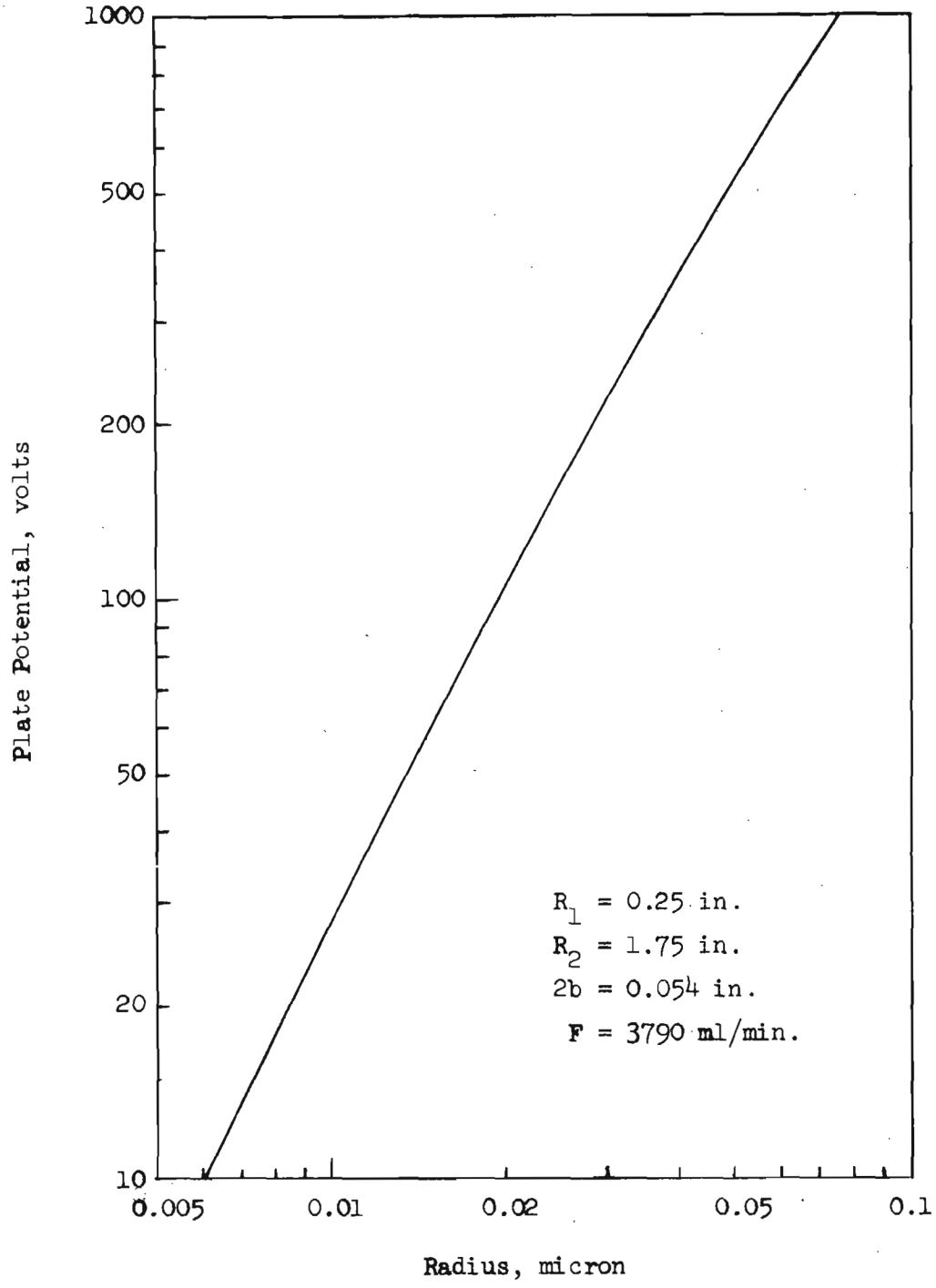
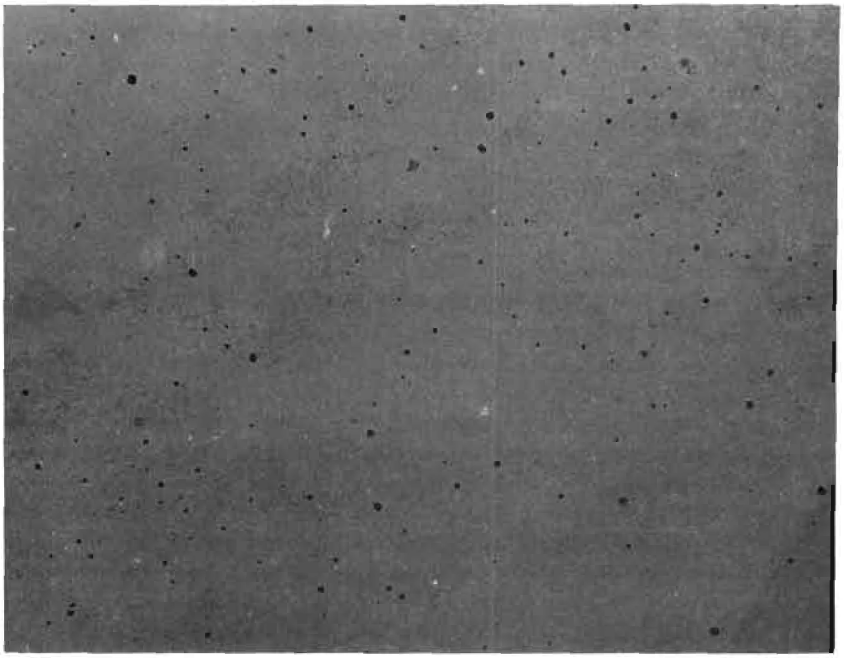


Figure 6. Correlation of Plate Potential and Particle Radius for Analysis of Ion Counter Data.

Samples were collected on two electron microscope grids placed at different locations along the radius in a radial thermal precipitator. Upon examination of these two grids it was determined that there was no statistical difference between the size distributions. There also appeared to be no evidence of significant particle agglomeration. Figures 7 and 8 are electron micrographs taken for aerosols with and without methylamine, respectively.

Size measurements were also made for aerosols under the same condition by ion counter. The size distribution obtained based on an actual separation between plates of 0.0787 inch agreed with the size distributions using micrographs and optical microscope counts over the small end of the distributions but departed noticeably over the large end. This was to be expected as a result of the assumption of a single electron charge on the particles. However, due to the construction of the ion counter, the method of measuring the separation between the plates was not as accurate as desired and there was no way of insuring that the plates would be perfectly parallel. On these grounds, therefore, it was decided to change arbitrarily the value of the separation between the plates in the calculations until a value was found that gave acceptable agreement between the mean radius calculated from ion counter data and that obtained from particle examination. This was accomplished with a separation between the plates of 0.054 inch. Figure 9 represents a comparison between a size distribution from the micrographs and that obtained assuming a separation between the plates of 0.054 inch. This separation was used as the effective value between the plates of the ion counter in processing all other experimental data.



RESIDENCE TIME = 4 MIN.
RELATIVE HUMIDITY OF AIR = 48%

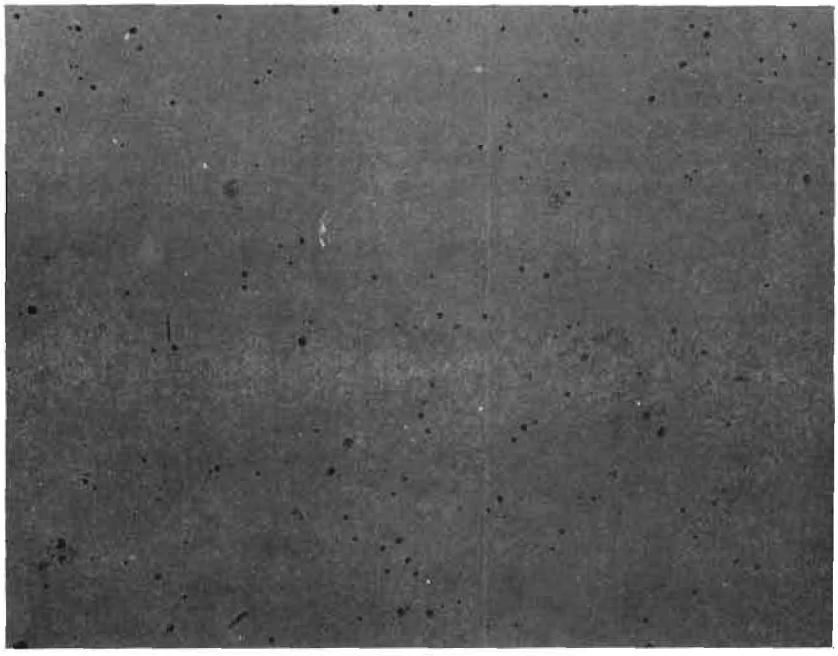
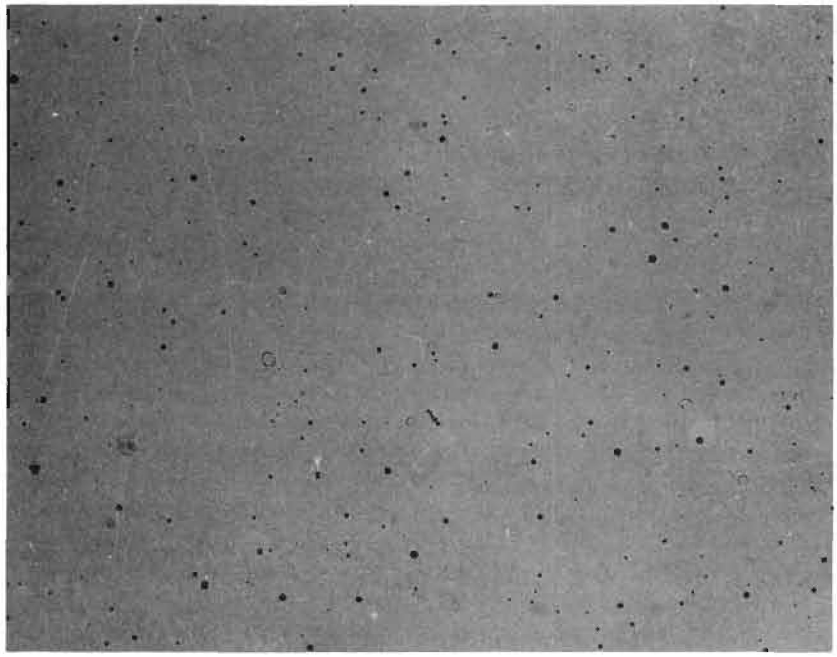


Figure 7. Micrographs of Sodium Chloride Particles from an Aerosol of Clean Air.



RESIDENCE TIME = 4 MIN.
RELATIVE HUMIDITY OF AIR = 48%

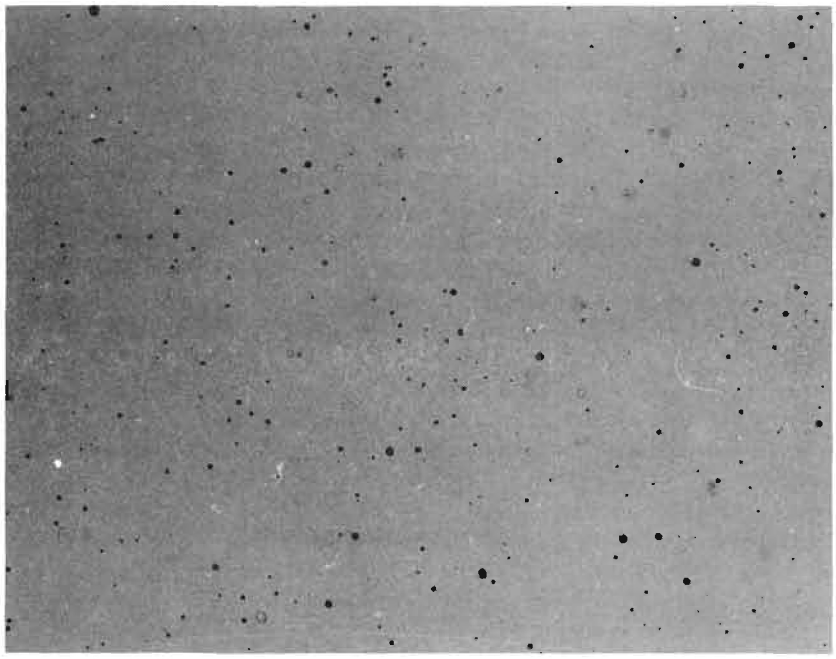


Figure 8. Micrographs of Sodium Chloride Particles from an Aerosol with a Trace of Methylamine.

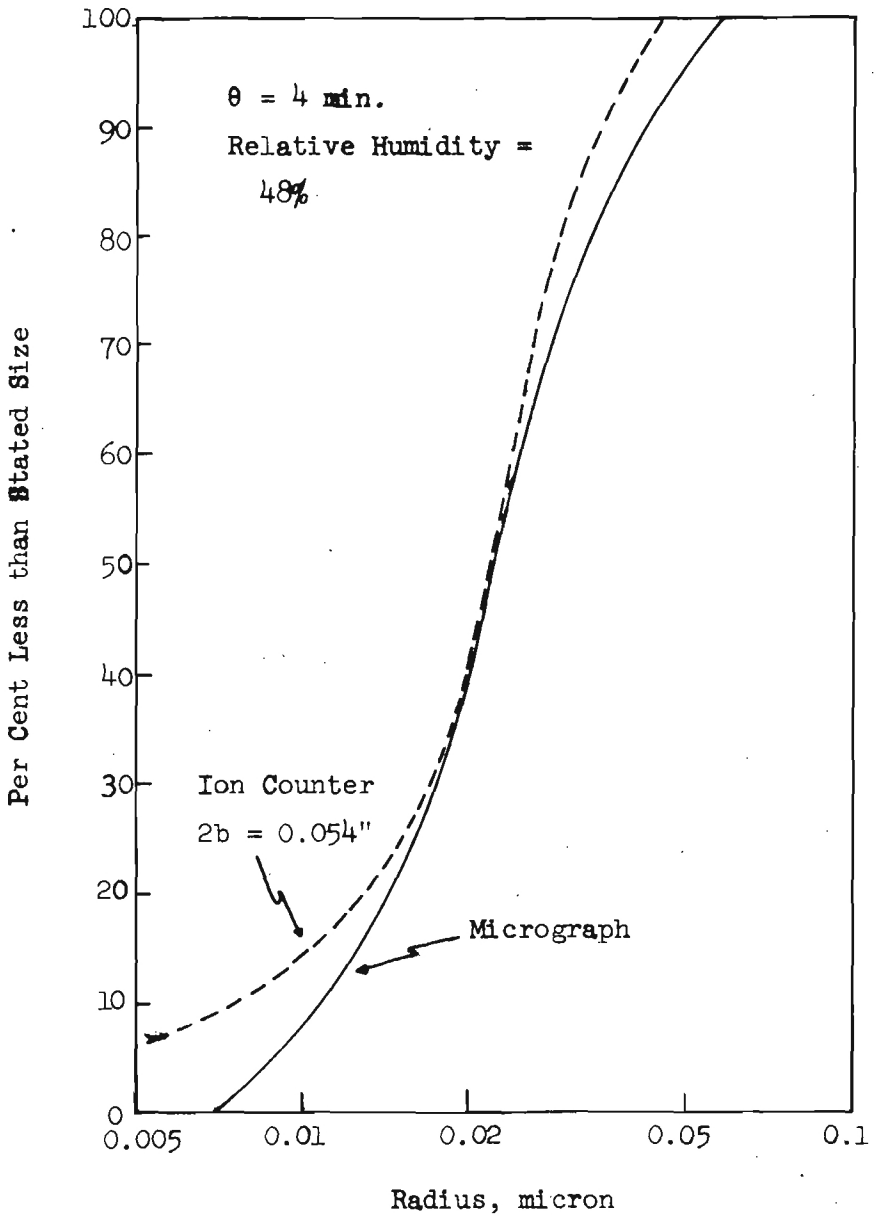


Figure 9. Comparison of Size Distributions Obtained from Ion Counter and Micrograph Data.

B. Comparison between systems with and without methylamine

An analysis was made to test whether or not the ion counter was suitable for systems containing methylamine. According to the theory, a small quantity of foreign vapor added to air should not affect the performance of the ion counter. Tests were made using aerosols with and without methylamine. Sodium chloride was in dry crystal form under the test condition so the initial aerosol particulate sizes should be identical. If the ion counter method was reliable, the sizes obtained should be the same. Results are shown in Figure 10; good agreement is obvious.

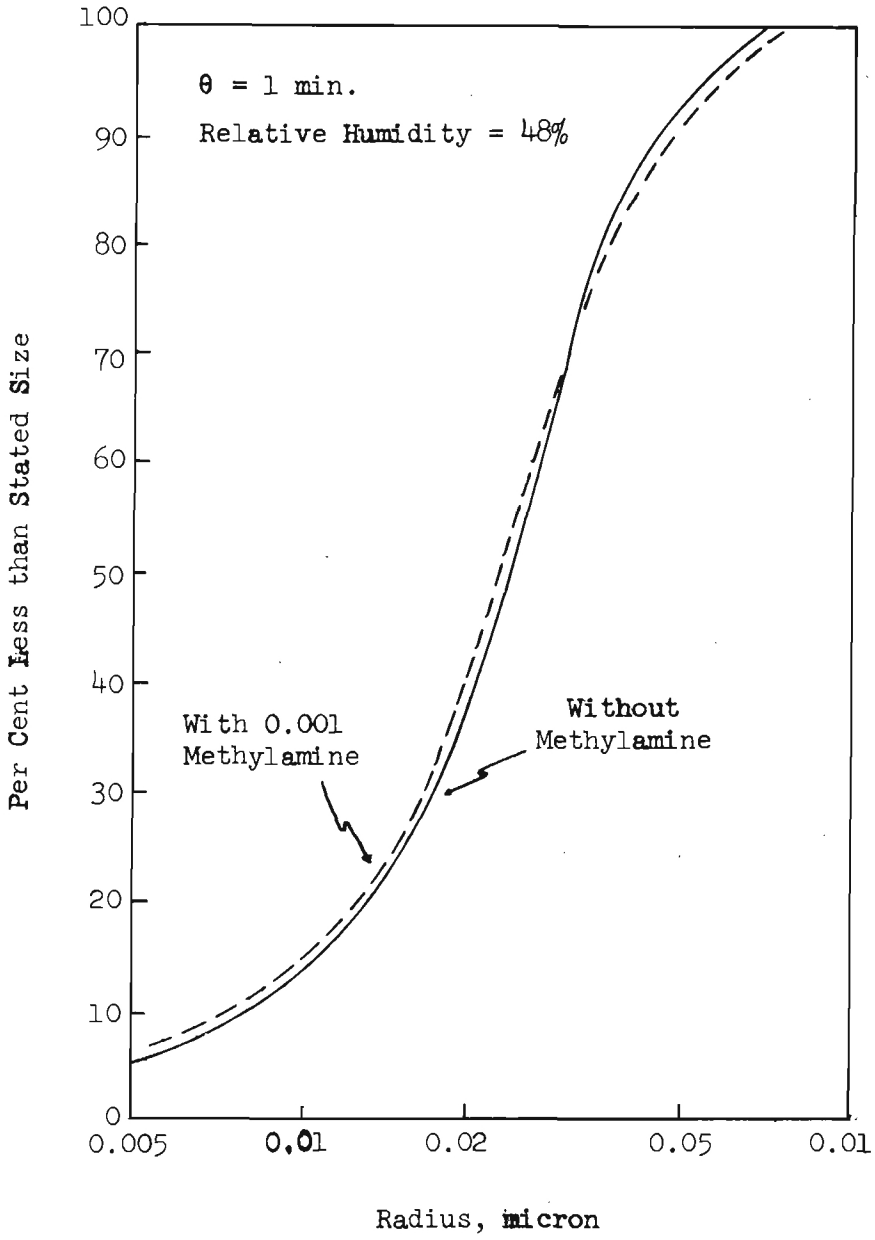


Figure 10. Comparison of Size Distributions Obtained from Ion Counter Data for Systems with and without Methylamine.

VI. SOLUBILITIES AND DISSOLUTION RATES OF SODIUM CHLORIDE IN AQUEOUS METHYLAMINE SOLUTIONS

Solubilities and dissolution rates of sodium chloride in water and aqueous methylamine solutions were measured experimentally. Two beakers of the same size were placed on an automatic shaker (Arthur H. Thomas Company, Philidelphia, Penn.) having a flat platform holder. Glue was used to insure firm contact between beakers and the platform. One beaker was filled with a known amount of distilled water. The other was filled with the same amount of aqueous methylamine solution of known concentration. The shaker was started first and then a small and equal amount of sodium chloride was added to both beakers at the same time. Times required to dissolve all the added sodium chloride in each beaker were recorded. More sodium chloride was added when the previously added quantity was dissolved and the same procedure was repeated until no more sodium chloride would dissolve. The portions not dissolved eventually were estimated by comparison to a similar quantity that could be weighed with a balance. The tests were repeated a number of times. The shaker was set at a constant speed for all tests. No difference was detected when the positions of the beakers were interchanged. Therefore, the measured rates of dissolution were deemed to be satisfactory for comparison of water and an aqueous methylamine solution.

The tests were conducted with distilled water and aqueous methylamine solutions from the Fisher Scientific Company. An equal amount of sodium chloride was added to each of the two beakers containing 100 ml of liquid and the time required to dissolve was recorded for each beaker. A second addition was made when all the first addition of salt was dissolved in

both beakers. It was difficult to measure to seconds when the last crystal disappeared so the time was recorded only to halves of a minute. Results are presented in Table I. The rate of dissolution is obviously retarded by the presence of the methylamine. Under the same test condition, it took only 7 minutes to dissolve 10 grams of sodium chloride in 100 ml water, but 9.5 minutes for 5 per cent and 102 minutes for 25 per cent aqueous methylamine solution.

The solubility of salt also decreases in aqueous methylamine solutions as concentration increases. These results are presented in Figure 11. The solubility of sodium chloride in distilled water was almost the same as reported in the handbooks. Its solubility in 25 per cent aqueous methylamine solution was less than one third of that value.

TABLE I

RATE OF DISSOLUTION OF SODIUM CHLORIDE

Amount of NaCl of Each Addition (grams)	Time Required to Dissolve All NaCl of Each Addition: 100 ml Distilled Water (min)	100 ml 5% Aqueous Methylamine Solution (min)
10	7	9.5
5	5	8.5
5	6	10
5	7	16
5	10	*
	100 ml Distilled Water (min)	100 ml 25% Aqueous Methylamine Solution (min)
10	7	102
1	3	113
1	3	**

* Only 2 g. dissolved overnight

** Only 0.5 g. dissolved overnight

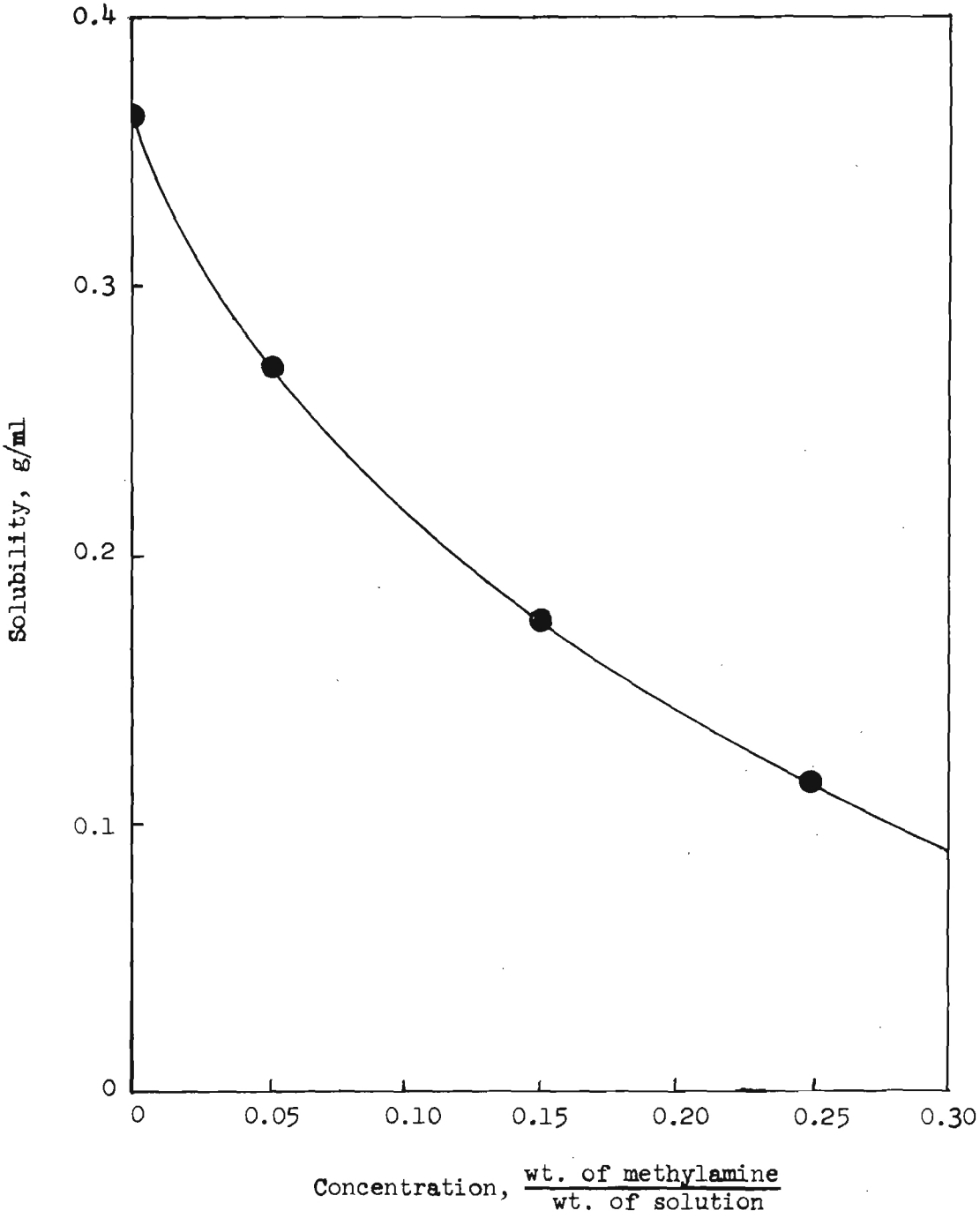


Figure 11. Solubility of Sodium Chloride in Aqueous Methylamine Solution.

VII. EFFECTS OF METHYLAMINE ON DEW POINT OF AIR

Methylamine gas for the experiments was obtained from the Matheson Company with a purity better than 98 per cent. The impurities in the gas were mostly high boiling point organic gases. They were removed to a large degree by means of an ice trap. The boiling point of methylamine at 1 atmosphere pressure is 20°F so that it did not condense in the ice trap. The arrangement for the dew point measurement is shown in Figure 12.

Air was let into the system at a constant flow rate, only a small portion of it being used in the dew point measurement. This flow rate was maintained constant throughout the tests. Methylamine was introduced into the system at the desired rate. Small diameter and thin-wall glass tubing was used and the temperature was brought to within half of a degree of that of the room before it entered the flowmeter. Dew point temperatures were measured at various methylamine concentrations. The dew point temperature of methylamine alone was also measured. Much longer times were found to be necessary for the hygrometer to yield a steady reading than for other cases. This was probably caused by water molecules remaining in the system. After all the air and water vapor that could be were removed from the system, the dew point measured for methylamine was very close to the value given in the handbooks. This indicated that the purity of the methylamine was satisfactory after treatment and that the dew point data were reliable.

Tests were made using air at three different humidity conditions. These were dew points of 55, 62, and 66°F. These results are presented in Figure 13. Condensation occurred in the system tubing when only 0.3 per cent of methylamine was added to the air having a dew point of 66°F at a room

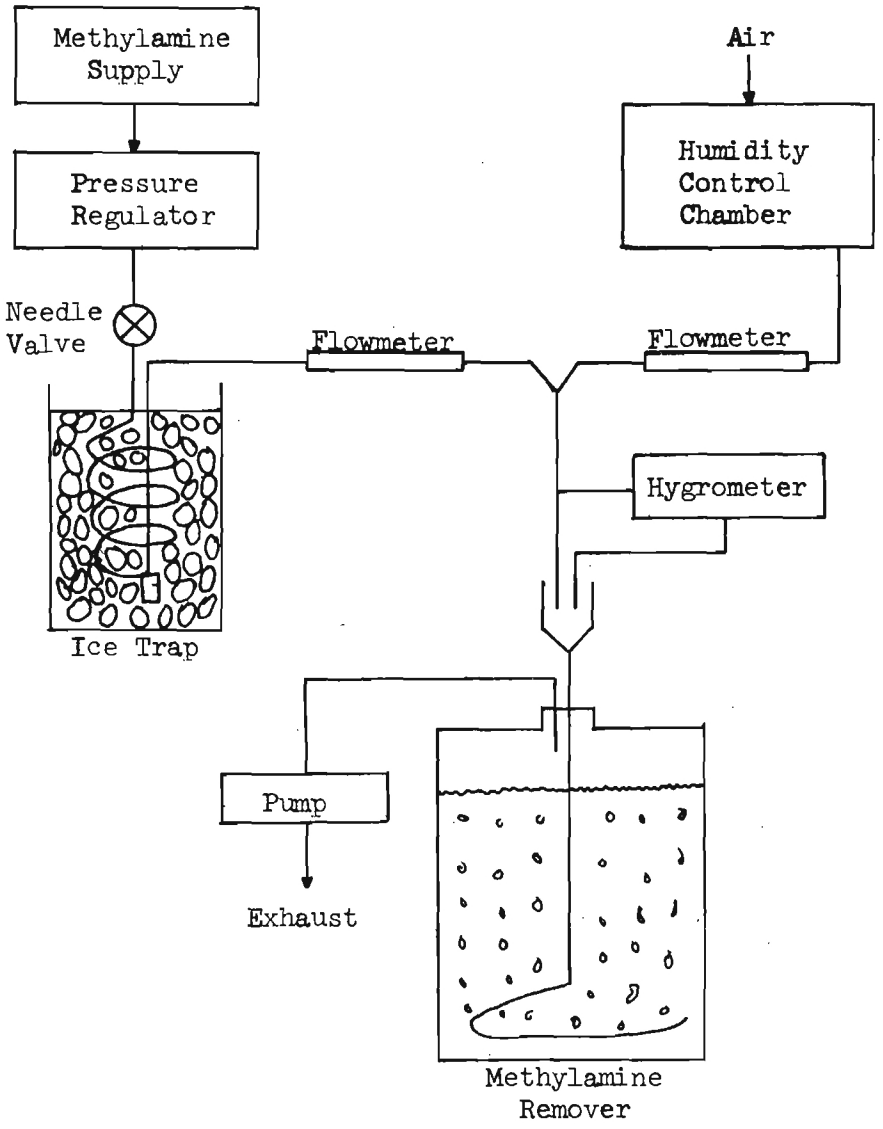


Figure 12. Experimental Arrangement of Dew Point Temperature Measurements for Air-Methylamine Systems.

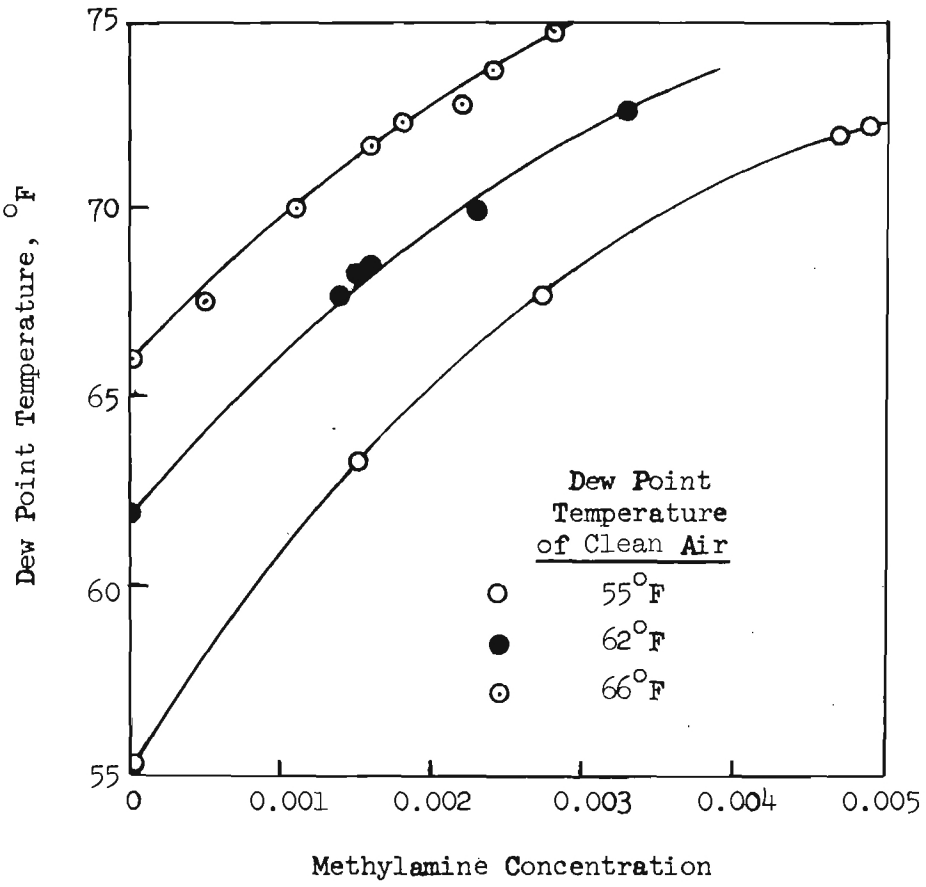


Figure 13. Effects of Methylamine in Air on the Dew Point Temperature.

temperature of 75°F. Condensation, if no methylamine was added, would not have occurred at temperatures above 66°F. The reason could either be that a chemical reaction occurred between the water and the methylamine forming a high boiling point compound or that water condensation was promoted by the methylamine through catalytic action, or both.

VIII. RESULTS AND DISCUSSION

Dry sodium chloride particles adsorb moisture in the air and their sizes increase noticeably at relative humidities above 75 per cent. The growth in particle size depends on the humidity of the air and the time allowed. The higher the relative humidity and the longer the residence time the larger the particles will grow. The term "dry crystals" is used here to mean sodium chloride particles having practically the same size as those in dry air. The adsorption of water molecules on the particle surface before a measurable change in size occurs is still considered to represent a dry crystal condition. The term "solution droplets" refers to particulates produced when the water condensed on their surfaces results in the particles going into solution. The term "particulates" is used to describe dry crystals, solution droplets, partially dissolved crystals and partially nucleated droplets. The term "growth" is used to describe the result when dry crystals are exposed to a relative humidity condition in a residence chamber higher than in the conditioning chamber where the temperature was sufficiently high to ensure that all particulates were dry crystals. The time which the particulates remain in a residence chamber, θ, is called "residence time". The relative humidity is determined by the dew point temperature of air, T_{DA}, and the residence chamber temperature, T_r. Since relative humidity is not defined when methylamine is present, data are generally presented as particulate size versus dew point temperature of air.

A. Hysteresis of sodium chloride particulates in air

Dry sodium chloride crystals become solution droplets very quickly when they are exposed to an environment having a relative humidity above

75 per cent. The growth rate of the particulates depends on the new humidity conditions. When solution droplets are exposed to an environment of relative humidity slightly below 75 per cent, they do not become dry crystals as quickly as they became droplets. For example, dry crystals of 0.0182 micron radius at 74 per cent relative humidity will grow into solution droplets of 0.025 micron radius in 15 seconds when they are exposed to an environment of 95 relative humidity. But when this process is reversed, solution droplets will evaporate and become droplets of 0.0225 micron radius instead of 0.0182 micron radius dry crystals in the same period of time. This phenomenon is called hysteresis.

The initial size of the solution droplets used in any evaporation rate study is very important. They must be as nearly identical as possible in order to produce comparable data. The initial radius of the solution droplets used in most of this study was 0.0255 ± 0.0005 micron as produced from 0.0182 ± 0.0003 micron radius dry crystals. The size of dry crystals was controlled by the atomizer and the size sharpening devices. The average size of the dry crystals was determined by many tests made at low relative humidities.

Hysteresis data are presented in Figure 14. The residence time was 15 seconds. Hysteresis was obvious because the solution droplets line does not follow the dry crystal line. It means that a longer time is required for a droplet to evaporate from a high relative humidity condition, A, and become a dry crystal at a low relative humidity condition, B, than for a dry crystal at B to grow into that droplet of the original size at A. In other words, if the aging time is fixed as shown in Figure 14, the particulate originating from the solution droplet condition is always larger than one

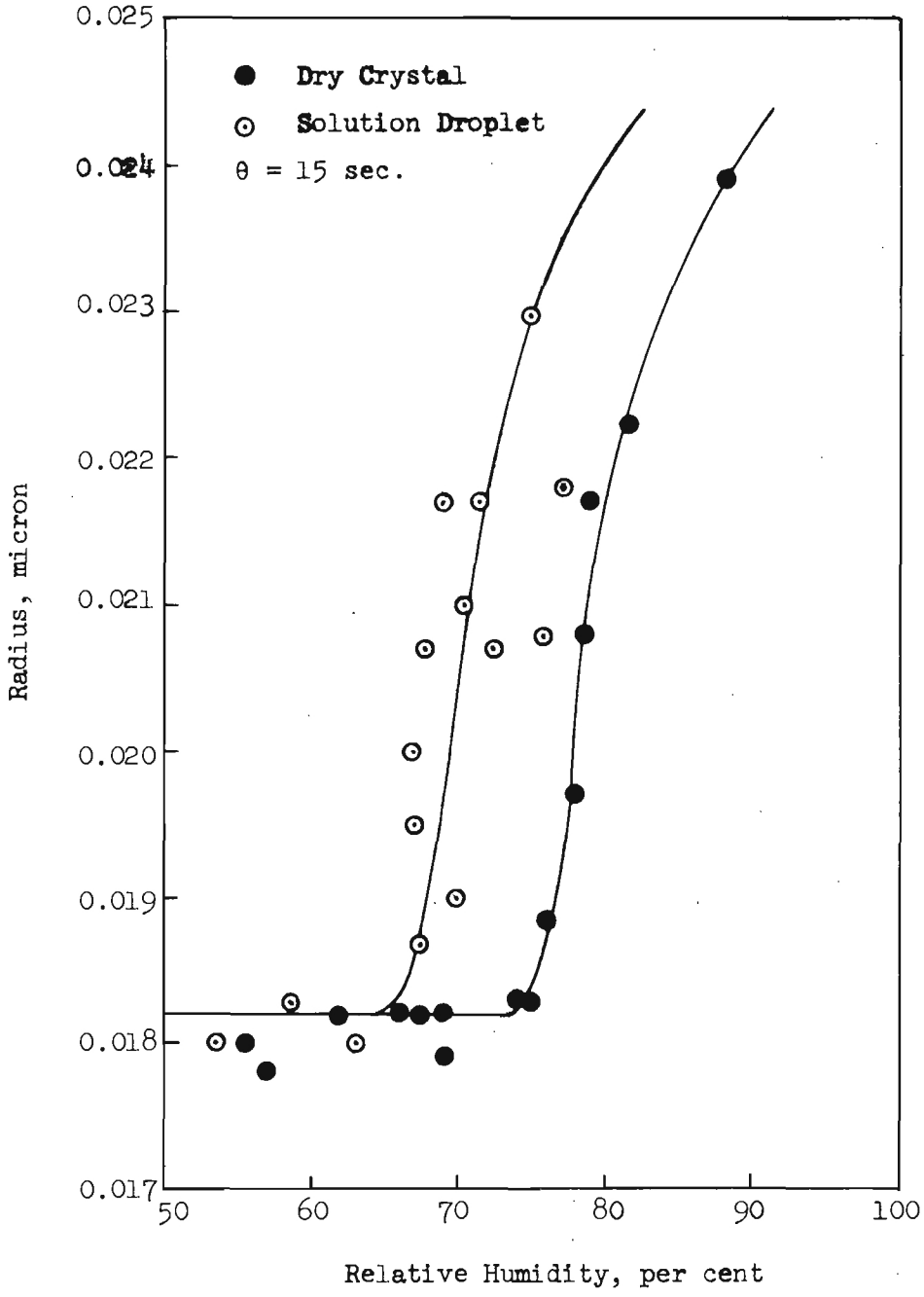


Figure 14. Hysteresis of Sodium Chloride Particulates in Air at Various Relative Humidities.

from the dry crystal condition at any relative humidity higher than 65 per cent. As residence time increases, the two curves of Figure 14 will become closer to one another and finally become one curve when the residence time is longer than the equilibrium time between the particulates and the environment. The curve is independent of the residence time at times greater than the equilibrium time.

Particulate sizes are plotted against dew point temperature in Figures 15 and 16. The curve for solution droplets is closer to the dry crystal curve for a residence time of 1 minute than it is for 15 seconds, as is to be expected.

B. Effect of methylamine on particulate size

Adding methylamine to air increases the dew point temperature of the air and promotes condensation. Methylamine in water decreases both the solubility of sodium chloride and the dissolution rate. The first characteristic causes more condensation on the particulate surfaces; the second retards both the rate at which sodium chloride dissolves in the water condensed on its surface and its solubility in the condensed aqueous methylamine solution.

Sodium chloride particles show no measurable size change when they come into equilibrium with an environment of less than about 75 per cent humidity. But when methylamine is present, sodium chloride crystals grow and become droplets when a certain concentration is reached. Figure 17 shows the size of the aerosol particulates in relation to the relative humidity of air and the concentration of methylamine. Methylamine has a dew point temperature of 20°F. The dotted lines shown on the figure indicate that condensation

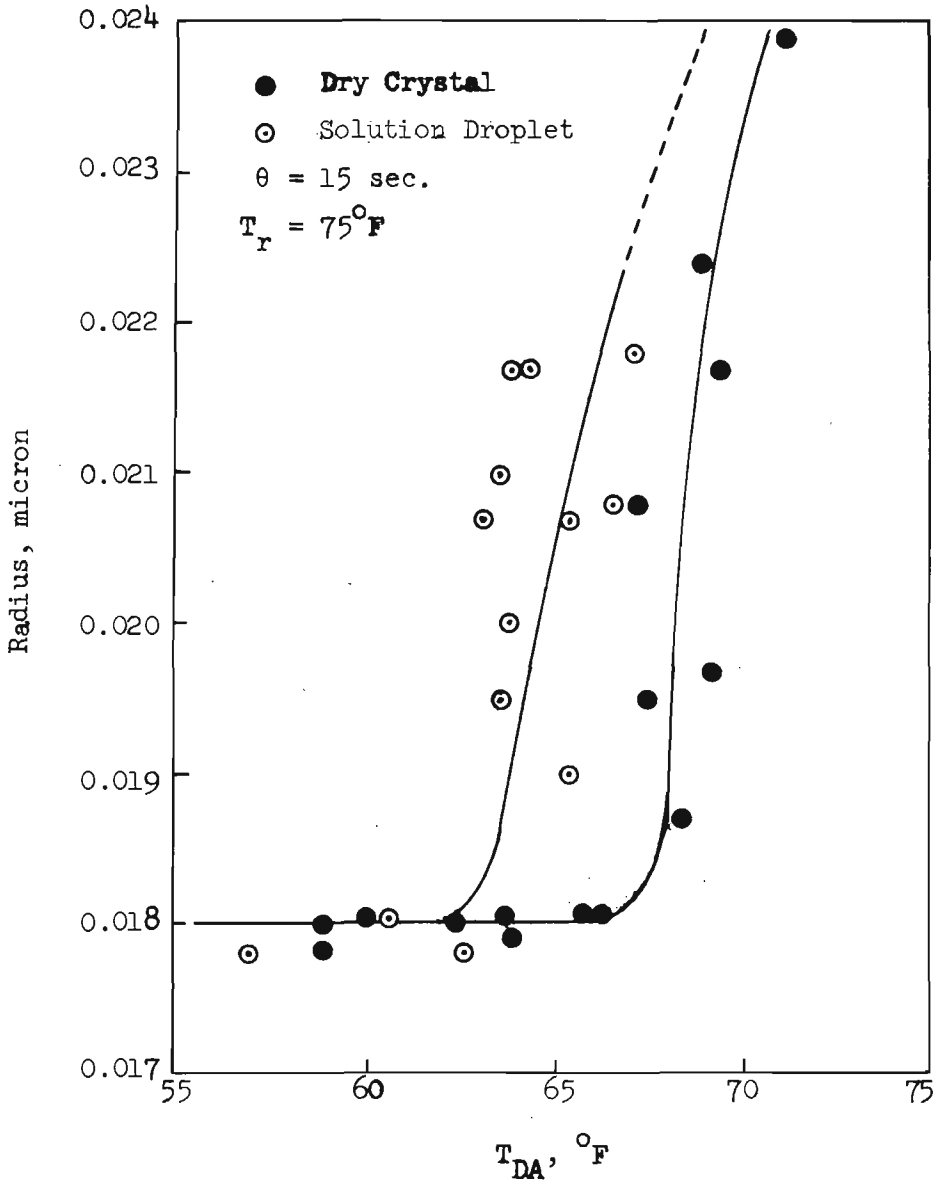


Figure 15. Growth and Evaporation of Sodium Chloride Particulates in Air with 15-Seconds Residence Time.

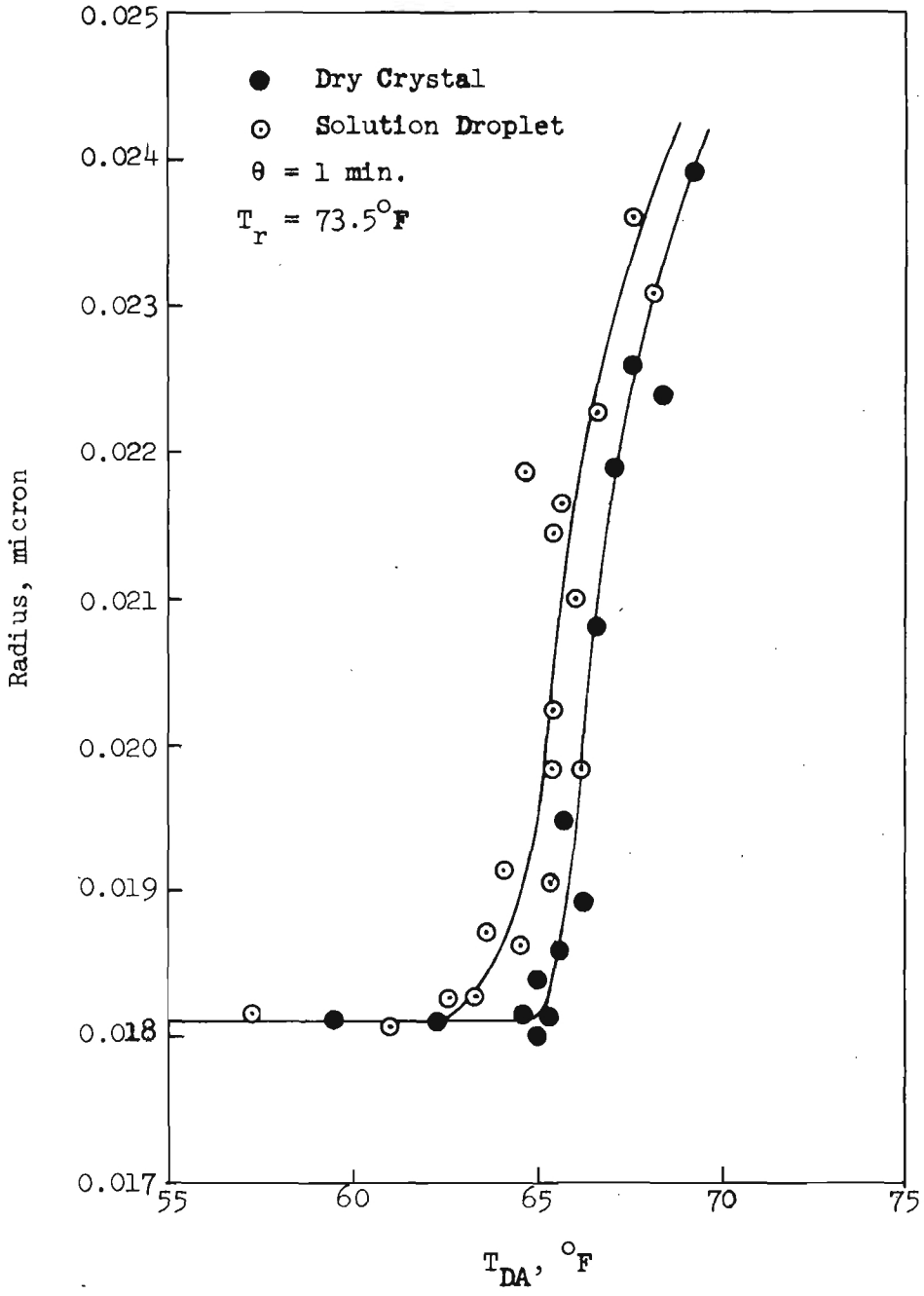


Figure 16. Growth and Evaporation of Sodium Chloride Particulates in Air with 1-Minute Residence Time.

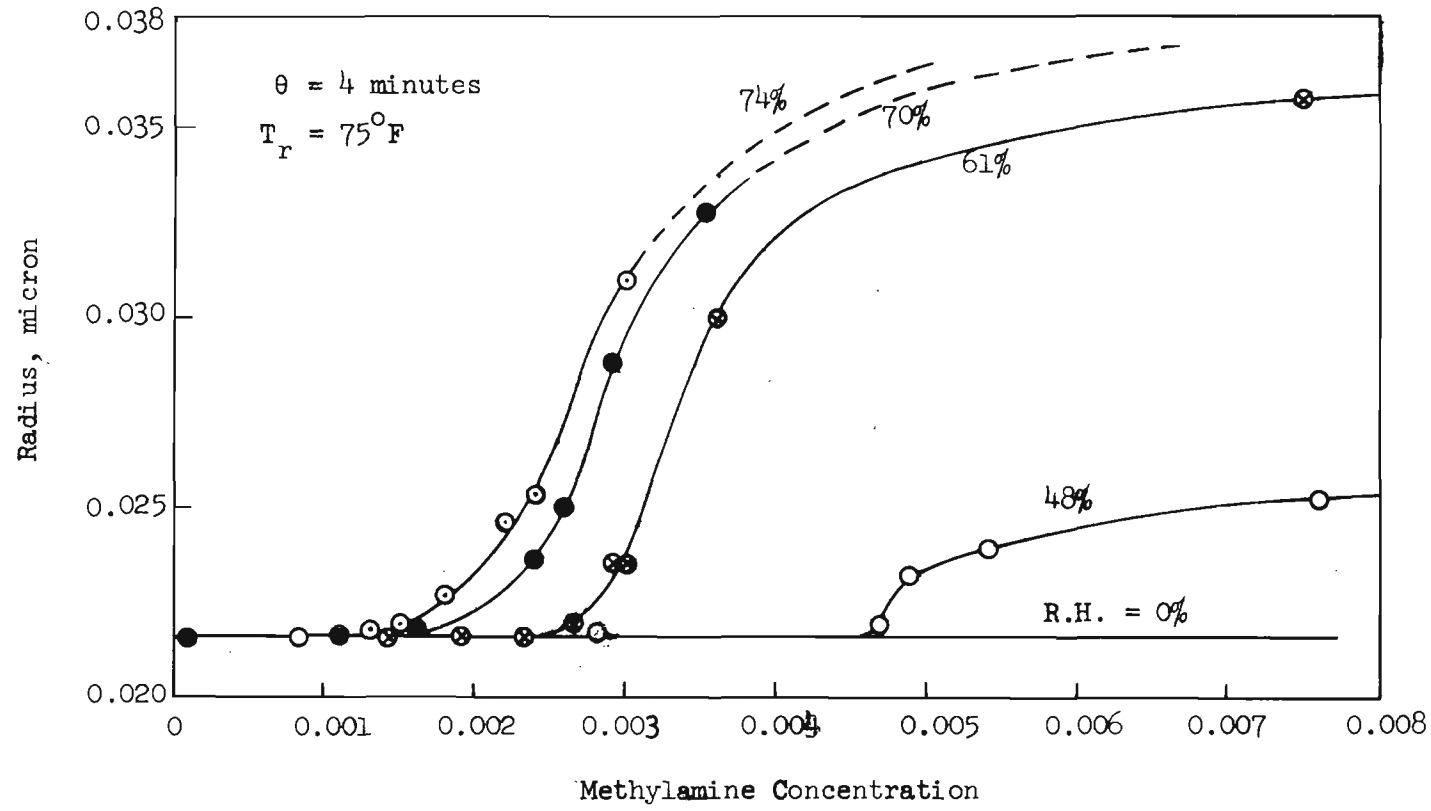


Figure 17. Growth and Evaporation of Dry Sodium Chloride Crystals in Air of Various Relative Humidities as a Function of Methylamine Concentration.

occurred on the glass wall of the chamber. It means that the dew point temperature of the aerosol had reached room temperature. The results show that the volume of liquid (mainly water) condensed on a sodium chloride particle is about twice the original volume of the dry crystal (0.0215 micron radius) when only 0.35 ml methylamine is added to 100 ml of aerosol having a relative humidity of 70 per cent. A dry crystal will grow 50 per cent in volume when 0.31 ml methylamine is added to 100 ml aerosol having a relative humidity of 61 per cent as shown in Figure 17. It would have not grown at all if the same volume of water vapor had been added to the aerosol.

Dry sodium chloride crystals will start to grow as the dew point temperature is brought up to about 70.5°F by adding methylamine. If water vapor instead of methylamine had been added to the aerosol to increase the dew point temperature, the crystals would start to grow at about 66.5°F.

Growth of dry sodium chloride crystals in air with and without methylamine (0.001 by volume) during a residence time of 15 seconds is presented in Figure 18 as a function of relative humidity. The results show no measurable differences between air and air-methylamine systems (0.001 concentration) when particulate size is plotted against the relative humidity of the air alone. The dotted line was plotted as size versus "apparent relative humidity" as obtained from a psychrometric chart using the dew point temperature of the aerosol after the methylamine was added. This indicates that sodium chloride crystals start to grow at a higher dew point temperature in air-methylamine systems than in clean air systems. The curve of size versus the relative humidity of clean air for air-methylamine systems shifts to lower relative humidities as concentration of methylamine increases. According to the results shown in Figures 13 and 17, when the

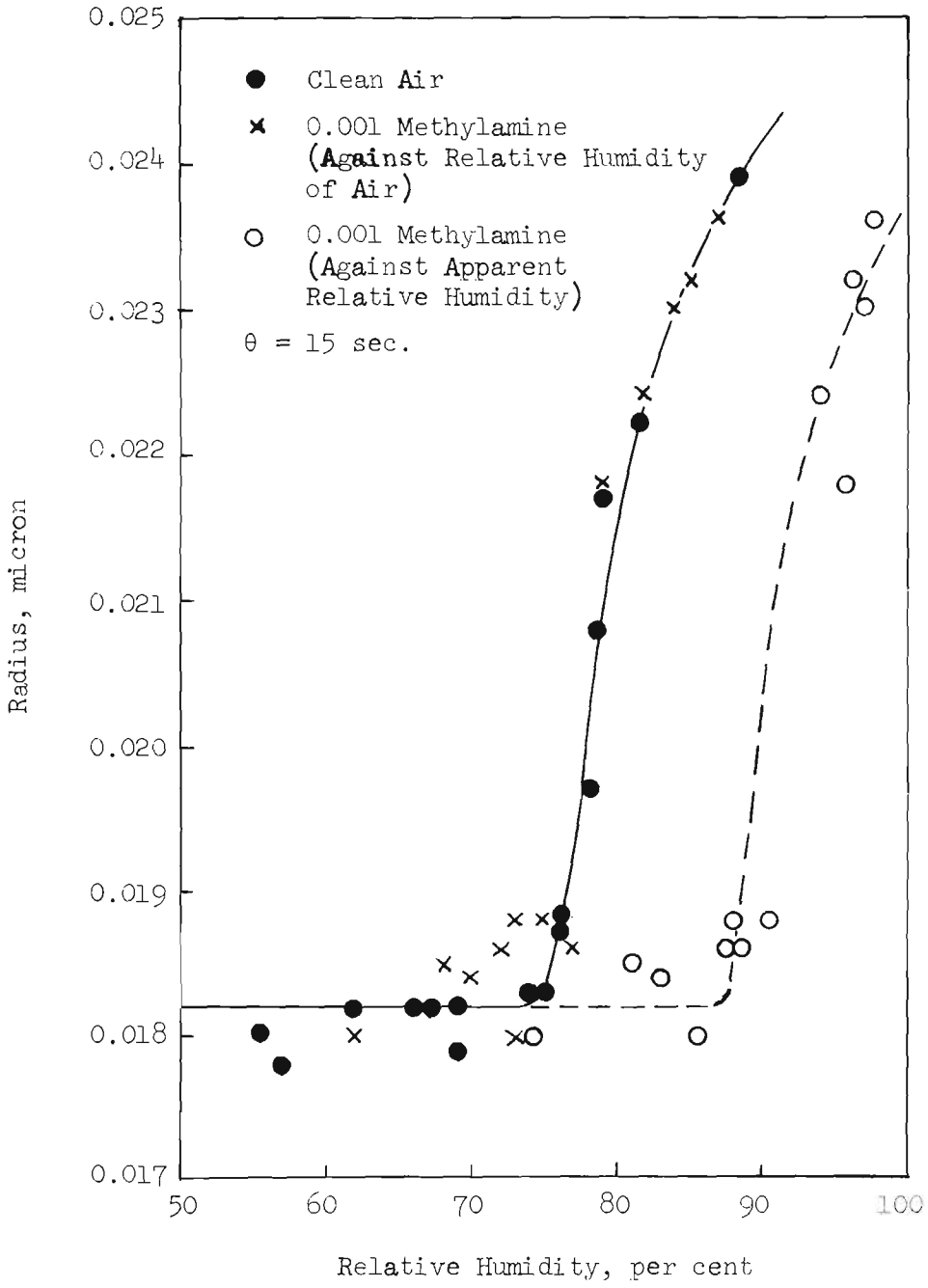


Figure 18. Growth of Dry Sodium Chloride Crystals in Air with and without Methylamine as a Function of Relative Humidity.

concentration of methylamine is doubled, i.e., increased from 0.001 to 0.002, the points (x on Figure 18) shift to about an 8 per cent lower relative humidity.

Growth curves for dry sodium chloride crystals in air and air-methylamine systems (0.0005 concentration) are presented in Figure 19 showing size versus the dew point temperature of the air alone. Radii of the particulates after aging one minute in air having a dew point temperature over 65°F were noticeably smaller than those aged in air of the same dew point temperature but with methylamine added. The actual dew point temperature of the aerosol was increased about two degrees after methylamine was added, however.

Hysteresis shown by sodium chloride particulates in air-methylamine systems is presented in Figure 20. The radii of particulates are plotted against dew point temperature before methylamine was added. Aerosols containing solution droplets were preconditioned in a humidity chamber at temperatures just slightly above the dew point temperature before entering the residence chamber. Sizes of the aged particulates from both initial conditions--dry crystal and solution droplet--were greater than those measured in air except when they were dry crystals after having aged.

The rate of growth of sodium chloride particulates is presented in Figure 21 as a function of the residence time. Initial conditions assured dry crystals for all tests. It was found that particulate sizes increased initially very rapidly in all cases. However, the equilibrium state seemed to be reached much sooner in air than in air with methylamine. The aerosol particulates were larger in air with methylamine than without it. The relative humidity was 80 per cent for the aerosol in all cases. Dew point temperatures for air-methylamine systems were higher, of course. This

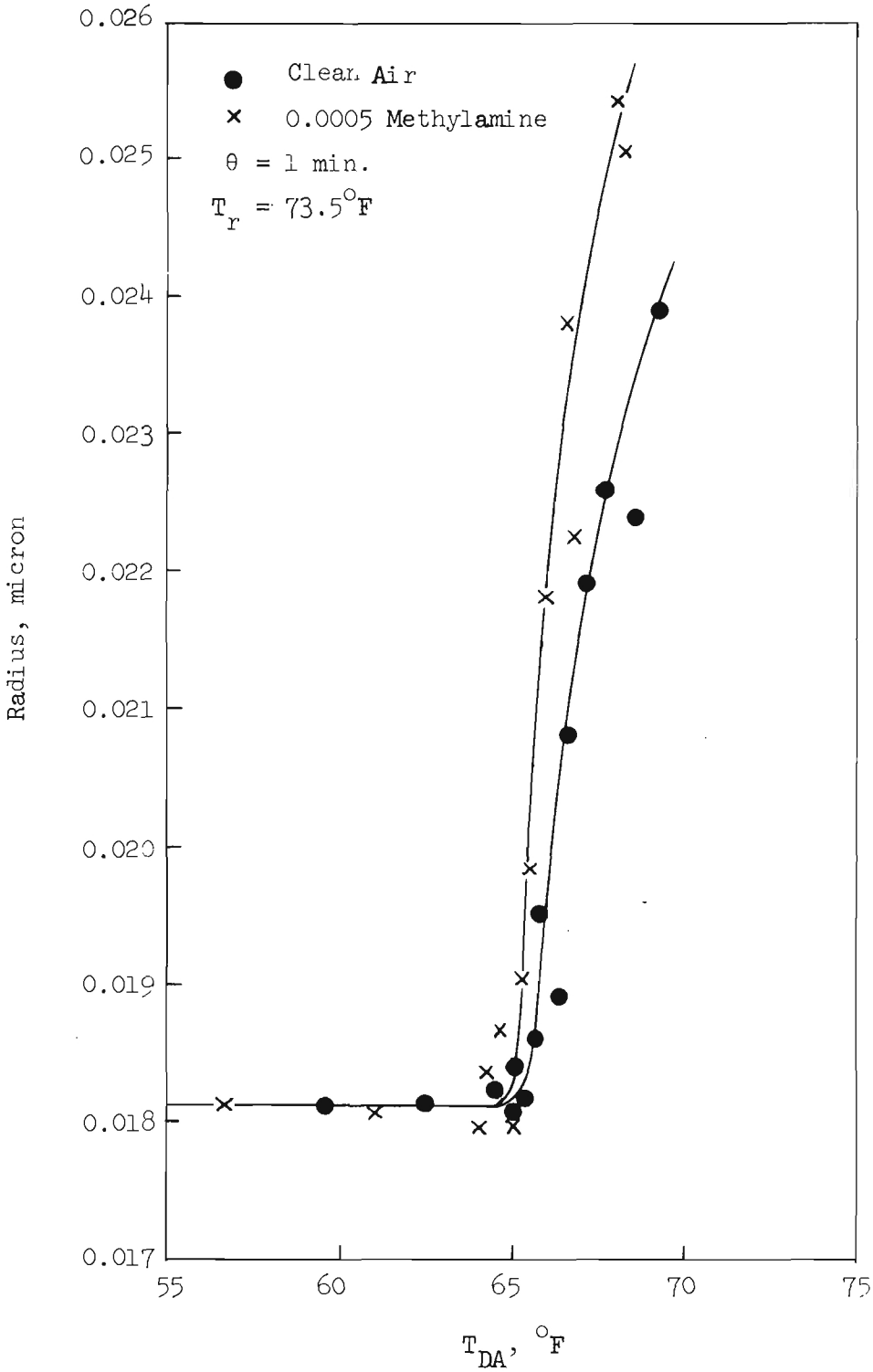


Figure 19. Growth of Dry Sodium Chloride Crystals in Air with and without Methylamine.

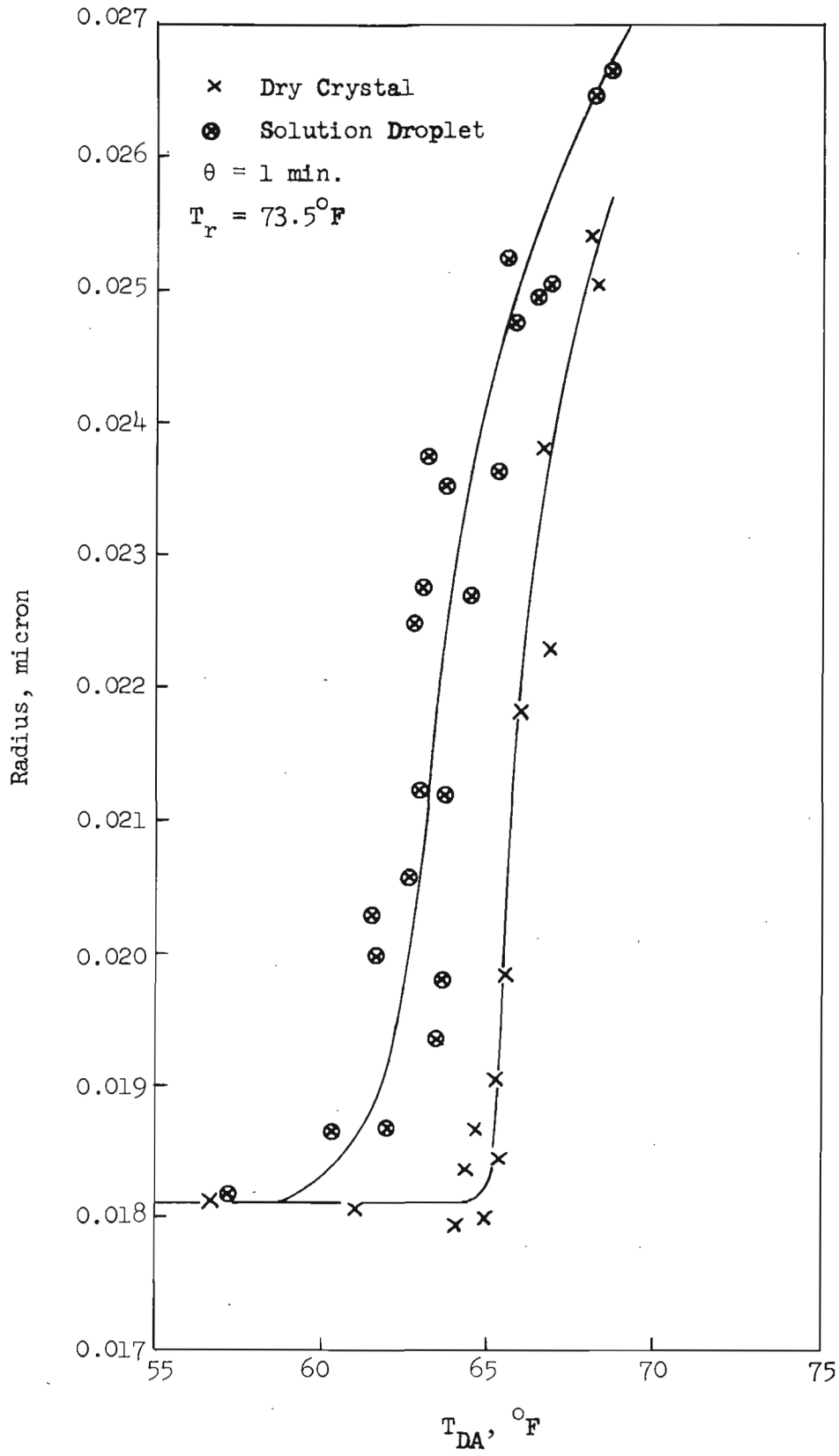


Figure 20. Hysteresis of Sodium Chloride Particulates in Air with Methylamine.

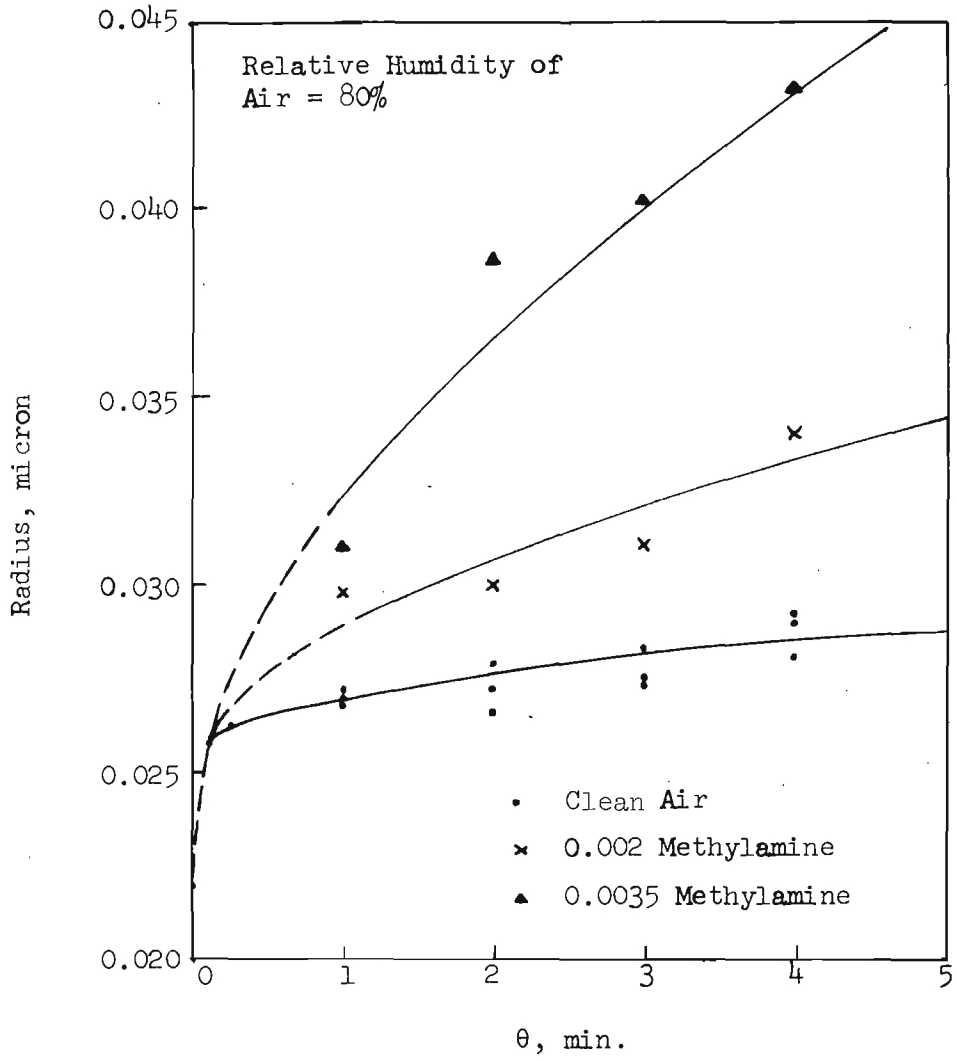


Figure 21. Size of Sodium Chloride Particulates in Air and Air-Methylamine Systems as Related to Residence Time.

probably explains why sizes were greater in air with methylamine. Equilibrium between particulates and the environment was achieved more slowly in air-methylamine systems probably due to the fact that the rate of dissolution and the solubility of sodium chloride were retarded by methylamine.

C. Effect of sulfur dioxide on particulate size

No measurable difference was detected in the dew point temperature of aerosols before and after sulfur dioxide was added. When the concentration of the sulfur dioxide was less than 0.001, the hysteresis displayed by sodium chloride particulates was about the same as in air. Small differences were detected when the sulfur dioxide concentration was increased to 0.005 by volume. Droplet sizes were consistently greater then and the evaporation rate was retarded. These results are presented in Figure 22. No difference was observed on the growth of dry crystals at this concentration. More tests are needed for air-sulfur dioxide systems before any final conclusion can be drawn.

D. Effect of other substances and tests with sea water

Tests were made by passing sodium chloride aerosols through a chamber containing ethanol, the aerosols picking up the ethanol vapor at room temperature. Particle size changes with humidity were no different from changes in air only. Tests were also made with aerosols generated from sodium chloride solutions saturated with Alpha-pinene. Solution was withdrawn from the bottom. No differences were detected here either.

Sea water was filtered through a Millipore filter and used to generate aerosols. As shown in Figure 23 the dry crystal size was larger than when generation was made using 0.05 per cent sodium chloride solution. This,

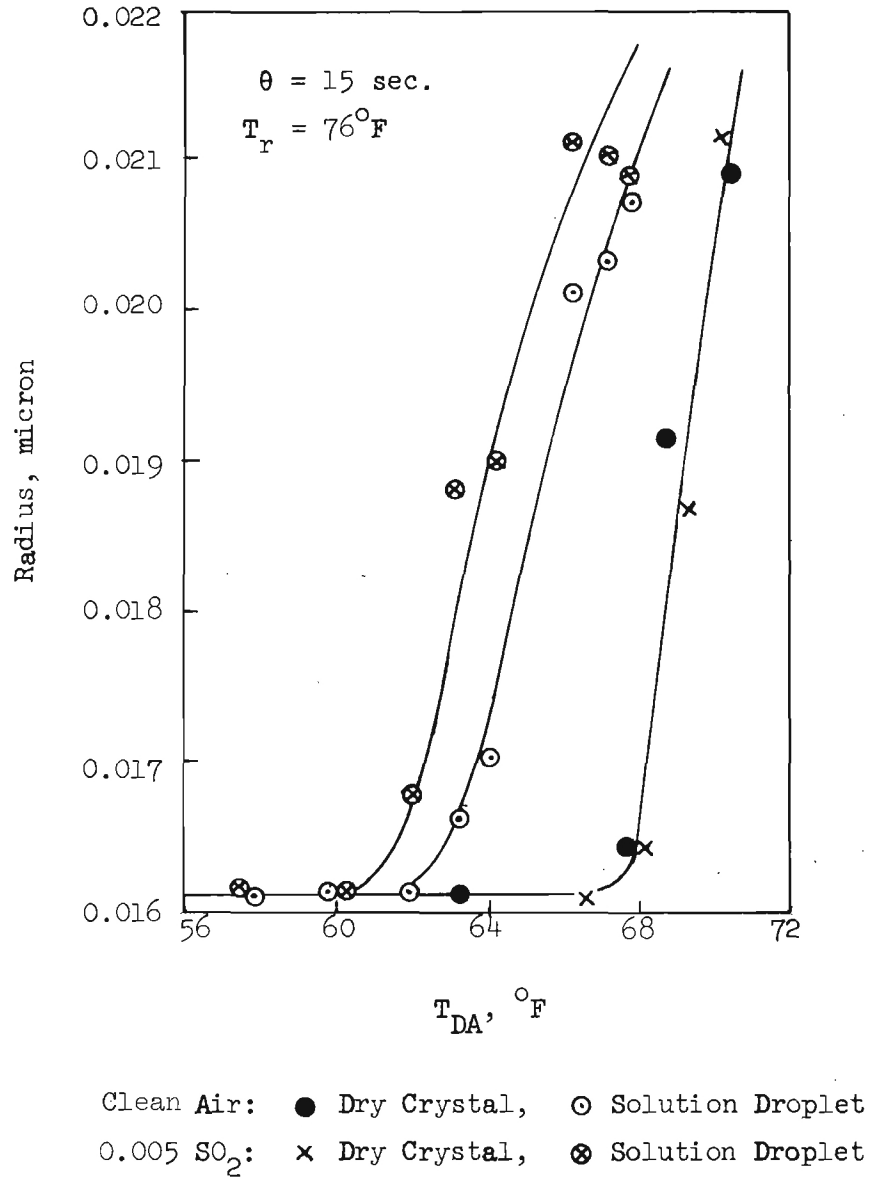


Figure 22. Growth and Evaporation of Sodium Chloride Particulates with and without Sulfur Dioxide.

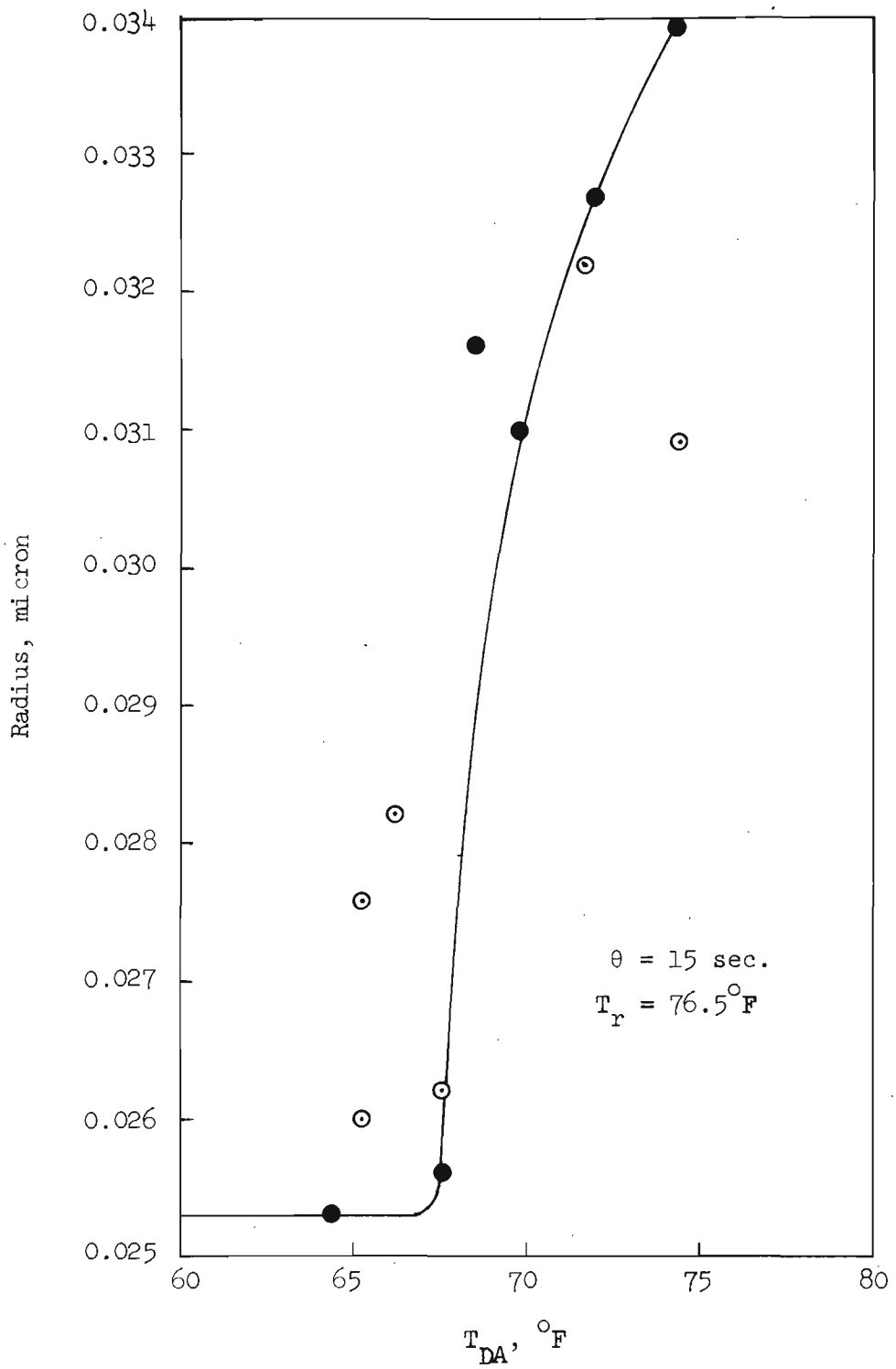


Figure 23. Results of Aerosol Generated from Sea Water.

of course, was due to the higher concentration of sodium chloride in sea water than in the laboratory solutions. The crystals produced by sea water behaved similarly to those generated by the 0.05 per cent sodium chloride solution. The results were somewhat more irregular and more tests were needed to establish a curve.

E. Discussion

The methods employed in these experiments were satisfactory for studying the behavior of sodium chloride particulates in air and in air containing impurities. There were limitations and difficulties, however. The size of the particulates was limited to about 0.01 to 0.05 micron in radius. The difference in size between the dry crystals and the solution droplets was quite small. Small defects or operational deficiencies in any part of the system during a series of tests caused significant uncertainties. Results of many tests were discarded because of faults traced to the aerosol generator, the size sharpening system, the ion counter, and to the accessory components. Extreme care had to be exercised throughout all the tests. All thermometers used in the system were calibrated against one standard. Flow meters were always cleaned and calibrated before a series a tests.

IX. CONCLUSIONS AND RECOMMENDATIONS

Conclusions derived from this research can be summarized as follows:

(1) Methylamine in air increases the dew point temperature and promotes condensation on sodium chloride particulates.

(2) Dry crystals of sodium chloride become solution droplets at a lower relative humidity condition in the presence of small concentrations of methylamine.

(3) Sodium chloride dissolves in aqueous methylamine solution much slower than in water. Solubility is lower, also. Therefore, dry crystals of sodium chloride become solution droplets at a higher dew point temperature in air containing methylamine than in air alone.

(4) Preliminary evidence suggests that sodium chloride solution droplets evaporate slower in air containing sulfur dioxide than in air alone. However, more data are needed before a definite conclusion is made. Growth rate results show no difference in air with and without sulfur dioxide.

(5) Ethanol vapor and Alpha-pinene do not affect evaporation and growth of sodium chloride particulates under the test conditions made in this study.

(6) Aerosols generated from sea water behave similarly to those generated from sodium chloride solutions prepared in the laboratory.

Recommendations for further research in this field are as follows:

(1) Foreign vapors were introduced before aerosols entered the humidity conditioning chamber in this study. It would be interesting to see whether or not different results would be obtained by adding the vapors

just before the aerosols entered the residence chamber. Droplets were somewhat larger when the methylamine was added before the humidity conditioning chamber in the present arrangement.

(2) More studies are needed with sulfur dioxide and other contaminates.

(3) Theoretical analysis is needed to aid in understanding more fully the growth of hygroscopic nucleii and the evaporation of solution droplets.

Respectfully submitted:

Clyde Orr, Jr.
Project Director

Approved:

Frederick Bellinger, Chief
Chem. Sci. and Materials Division

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